Published Monthly. Price, $5.00 per Annum.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

VOL. XX.—NO. 5.

MAY, 1898.

EDWARD HART, Editor, J. H. LONG, THOMAS B. OSBORNE,
COMMITTEE ON PAPERS AND PUBLICATIONS.

CONTENTS.

PAGE.

Proceedings ..... (35)-(50)

PAPERS.

The Oxyhalides of Zirconium. By F. P. Venable and Charles Baskerville 321

Atropine Periodides and Iodomercurates. By H. M. Gordin and A. B. Prescott 329

Composition of the Ashes of Some Raw Tanning Materials. By Wm. K. Alsop and J. H. Yocum 338

On the Determination of Potash without the Previous Removal of Iron, Calcium, etc. By C. C. Moore 340

The Determination of Methane, Carbon Monoxide, and Hydrogen by Explosion in Technical Gas Analysis. By W. A. Noyes and J. W. Shepherd 343

Proteids of the Pea. By Thomas B. Osborne and George F. Campbell 348

Proteids of the Lentil. By Thomas B. Osborne and George F. Campbell 362

On the Speed of Coagulation of Colloid Solutions. By C. E. Linebarger 375

New Books; Das optische Drehungsvermögen organischer Substanzen und dessen praktische Anwendung; Spectrum Analysis; On Laboratory Arts; The Arrangement of Atoms in Space; Bibliography of the Platinum Group, 1748–1896; The Calorific Power of Fuels; Methods for the Analysis of Ores, Pig Iron, and Steel; Text-book of Physical Chemistry 381

Books Received 392

REVIEW OF AMERICAN CHEMICAL RESEARCH 53-60

EASTON, PA.:
CHEMICAL PUBLISHING COMPANY.

Entered at the Post Office, Easton, Pa., as Second Class Matter.

Everything intended for insertion in the Journal should be addressed to the Editor, Edward Hart, Easton, Pa. Orders for back numbers of the Journal should be addressed to the Librarian, F. E. Dodge, 316 Bowne Ave., Flushing, N. Y.

OFFICERS OF THE AMERICAN CHEMICAL SOCIETY.

President: Charles E. Munroe, Columbian Univ., Washington, D. C.
Vice-Presidents: The Presiding Officers of the Local Sections; see below.
Secretary: Albert C. Hale, 551 Putnam Ave., Brooklyn, N. Y.
Treasurer: C. F. McKenna, 221 Pearl st., N. Y. City.
Librarian: F. E. Dodge, 316 Bowne Ave., Flushing, N. Y.
Committee on Papers and Publications: Edward Hart, Editor; J. H. Long; Thomas B. Osborne.
Committee on Nominations to Membership: A. A. Breneman; P. T. Austen; C. A. Doremus.
Finance Committee: Durand Woodman; A. P. Hallock; A. H. Sabin.
Directors. Members ex-officio: Charles E. Munroe, Pres.; Albert C. Hale, Sec. *Term expires December, 1898:* C. A. Doremus, C. B. Dudley. *Term expires December, 1899:* C. F. Chandler, Wm. McMurtrie.
Council. Members ex-officio: Charles E. Munroe, Pres.; Albert C. Hale, Sec.; Edward Hart, Editor. *Term expires December, 1898:* J. W. Mallet, Thomas H. Norton, G. C. Caldwell, C. F. McKenna, F. E. Dodge, H. W. Wiley, C. A. Doremus, A. A. Breneman. *Term expires December, 1899:* C. F. Chandler, H. L. Wells, Wm. McMurtrie, W. A. Noyes, P. T. Austen, Charles B. Dudley, Albert B. Prescott. *Term expires December, 1900:* G. F. Barker, F. W. Clarke, W. L. Dudley, A. A. Noyes.
Local Sections. Rhode Island Section: Edward D. Pearce, Pres. Officer; Walter E. Smith, Sec., 47 Jenkins St., Providence, R. I. *Cincinnati Section:* O. W. Martin, Pres. Officer; S. Waldbott, Sec., Lloyd Library, 224 W. Court St., Cincinnati, O. *New York Section:* Wm. McMurtrie, Pres. Officer; Durand Woodman, Sec., 127 Pearl St., N. Y. City. *Washington Section:* Henry N. Stokes, Pres. Officer; Wm. H. Krug, Sec., U. S. Dept. of Agr., Washington, D. C. *Lehigh Valley Section:* Jos. W. Richards, Pres. Officer; Bernard Enright, Sec., 330 E. 4th St., So. Bethlehem, Pa. *New Orleans Section:* A. L. Metz, Pres. Officer; Hubert Edson, Sec., Bartels, La. *Nebraska Section:* H. H. Nicholson, Pres. Officer; John White, Sec., Box 675, Lincoln, Neb. *Chicago Section:* J. P. Grabfield, Pres. Officer; F. B. Dains, Sec., 2421 Dearborn st., Chicago, Ill. *North Carolina Section:* F. P. Venable, Pres. Officer; W. A. Withers, Sec., A. and M. College, Raleigh, N. C. *Columbus Section:* H. A. Weber, Pres. Officer; Wm. McPherson, Sec., Ohio State Univ., Columbus, O. *North Eastern Section:* Arthur A. Noyes, Pres. Officer; W. R. Whitney, Sec., Mass. Inst. Tech., Boston, Mass.

PAPERS ACCEPTED FOR PUBLICATION:

Electrical Disturbances in Weighing. By H. K. Miller.

Analytical Notes upon the Estimation of Phosphorus in Steel. By R. W. Mahon.

Some Further Applications of Hydrogen Peroxide to Quantitative Analysis. By Percy H. Walker.

On the Decomposition of Concentrated Sulphuric Acid by Mercury at Ordinary Temperatures. By Chas. Baskerville and F. W. Miller.

Proteids of the Vetch. By Thomas B. Osborne and George F. Campbell.

Proteids of the Horse Bean. By Thomas B. Osborne and George F. Campbell.

Proteids of the Soy Bean. By Thomas B. Osborne and George F. Campbell.

Copyright, 1898, by Edward Hart, John H. Long, and Thomas B. Osborne, Committee on Papers and Publications of the American Chemical Society.

VOL. XX. [MAY, 1898.] NO. 5.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

[CONTRIBUTIONS TO THE CHEMISTRY OF ZIRCONIUM, NO. 9.]

THE OXYHALIDES OF ZIRCONIUM.

BY F. P. VENABLE AND CHARLES BASKERVILLE.

Received March 12, 1898.

I. ZIRCONIUM OXYCHLORIDES.

WE have examined three of these. The first is secured by the evaporation of an aqueous solution of the salt obtained by dissolving zirconium hydroxide in hydrochloric acid. Very large handsome crystals can be secured on slow evaporation over sulphuric acid. These crystals easily dry on porous plates or on filter-paper. Analysis gave:

Zr	28.05
Cl	21.59
Loss	50.46

This loss represents both water and combined hydroxyl or oxygen. These figures correspond to the formula $ZrOCl_2.8H_2O$. One difficulty in the way of securing a correct analysis lies in the constant loss of water on standing exposed to the air. This loss is shown in the following weighings:

	Dates.					
	Oct. 9.	Oct. 11.	Oct. 12.	Oct. 13.	Oct. 15.	Oct. 18.
Weighings	1.2806	1.2796	1.2792	1.2787	1.2779	1.2758

By heating to 135°–140° for six hours a large amount of chlorine is driven off and yet not all of the water. The mass is left only partly soluble. Heated to 100° under a stream of hydrogen chloride the weight was constant and the loss corresponded to

26.84 per cent. of the original weight. The residue is entirely soluble in water. Five molecules of water are thus lost at 100°, and the compound left is $ZrOCl_2.3H_2O$. This formula was confirmed by determinations of both ZrO_2 and Cl. The first formula, $ZrOCl_2.8H_2O$, is the one assigned by Paykull[1] and confirms his results as against those of Melliss.[2] The formula gotten by Herrmann, $ZrOCl_2.9H_2O$, was manifestly obtained from imperfectly dried crystals.

Various experiments on the dehydration of this salt were carried out. Thus a portion placed in a desiccator over fused calcium chloride had lost a large part of its water and was still losing weight after seven months. Another portion was placed over fused calcium chloride and dry air was drawn over it at the rate of about fifty liters in the twenty-four hours for six months. After the first two months it was examined weekly by the interposition of a flask containing silver nitrate to see whether hydrochloric acid was still coming off. Even after the lapse of so long a time as this it was found that the loss of hydrochloric acid continued although it was very slight. Lastly a portion was placed over concentrated sulphuric acid and the atmosphere above it exhausted occasionally. This was kept up during two months of summer weather. The loss in the last fifteen days was about 0.02 per cent. of the whole. The mass was powdery with a slightly discolored crust. It was all soluble in water, however, and yielded a clear, colorless solution. It contained 53.30 per cent. of zirconium dioxide. This corresponds very nearly to the formula $ZrOCl_2.3H_2O$.

Another form of the oxychloride is gotten by crystallization from concentrated hydrochloric acid. The form of the crystals is apparently similar to that of the crystals from an aqueous solution. It is difficult to free these from excess of acid. Linnemann,[3] by treatment of this with alcohol and ether, secured a fine, crystalline, snow-white, silky body, leaving fifty per cent. of its weight on ignition. This is, however, far from an accurate method for removing the water.

[1] *Ber. d. chem. Ges.*, **6**, 1467.
[2] *Ztschr. Chem.* (2), **6**, 196.
[3] *Chem. News*, **52**, 224.

Bailey[1] tried various methods of drying these crystals without success.

It was found that these crystals could be dried under hydrogen chloride at 100°–125° C. At this temperature a white mass soluble in water was gotten which gave on analysis :

	Calculated for $ZrOCl_2.3H_2O$.	Found.
Zr	39.12	38.99
Cl	30.66	29.98

The amorphous (?) form, insoluble in concentrated hydrochloric acid, but easily soluble in water, has been analyzed by Paykull, and he has calculated the formula $2ZrOCl_2.13H_2O$. This insoluble oxychloride is nearly always present during the process of purification by recrystallization from concentrated hydrochloric acid. Repeated boilings with hydrochloric acid fail to dissolve it. A sample was prepared by allowing a very concentrated aqueous solution of the oxychloride to fall drop by drop into concentrated hydrochloric acid. It was washed with hydrochloric acid and then boiled with it. After pouring off the acid the mass was washed with a mixture of nine parts ether and one part alcohol. It was dried between filter-paper. Little assurance could be felt that this mode of drying removed all the hygroscopic moisture. It was analyzed in this condition. Another portion was placed over caustic alkali (after pressing between filter-paper) and yet another portion was dried at 105° in a stream of hydrogen chloride.

The analysis of the portion dried between filter-paper was as follows (no difference was observed in that over caustic alkali after two days) :

	Calculated for $ZrOCl_2.6H_2O$.	Found.
Zr	31.70	31.72
Cl	21.01	20.81

This is therefore in close accord with the formula $ZrOCl_2.6H_2O$. The portion dried under hydrogen chloride was small and only the zirconium was determined. The percentage of this corresponded fairly well with $ZrOCl_2.3H_2O$.

Summarizing our examination of these oxychlorides then, we find that there are three :

[1] *Chem. News*, 60, 17.

1. An oxychloride gotten in large, well-formed crystals by crystallization from water. These crystals lose both water and hydrochloric acid on exposure to the air. Their formula is $ZrOCl_2.8H_2O$.

2. An oxychloride gotten by precipitation with hydrochloric acid from an aqueous solution. This is insoluble in hydrochloric acid. It is seen in silky crystals or a white mass of very fine crystals. The formula is $ZrOCl_2.6H_2O$.

3. An oxychloride gotten by crystallization from hydrochloric acid. This has the formula $ZrOCl_2.3H_2O$.

When any one of these is dried at 100°–125°, with a stream of dry hydrogen chloride passing over it, three molecules of water of crystallization are left and the oxychloride has the formula given under 3, namely $ZrOCl_2.3H_2O$. These last molecules of water are lost at a temperature of 180°–210°.

Weibull[1] gives the measurements of the crystals of the oxychloride formed from water. They belong to the tetragonal system, and are optically uniaxial with double refraction.

Several times during the examination of these oxychlorides the formation of a hydrogele was observed. The exact conditions under which it was formed were not determined. The tendency to form this hydrogele is much less than in the case of the bromides and iodides. Similar compounds will be mentioned there.

II. ZIRCONIUM OXYBROMIDES.

Zirconium oxybromides may be formed by decomposing the tetrabromide with water and also by dissolving zirconium hydroxide in hydrobromic acid.[2] It crystallizes from the aqueous solution in fine, transparent, needle-like crystals containing water of crystallization.[3]

Weibull gives the following analyses:

	Calculated for $ZrOBr_2.8H_2O$.	Found. I.	Found. II.
Zr	21.87	20.35	20.83
Br	39.05	41.16	38.70

He says that the crystals are isomorphous with those of the oxy-

[1] *Ber. d. chem. Ges.*, *1887*, 1394.
[2] Berthemot: *Ann. chim. phys.*, **44**, 393.
[3] Weibull: *Ber. d. chem. Ges.*, *1887*, 1394.

chloride which seems to be true. They are much more hygroscopic. His two analyses are decidedly discordant and one would judge that the amount of water of crystallization had been decided upon from the analogy to the oxychloride.

The oxybromides described in the following experiments belong to two types with varying degrees of hydration—$ZrOBr_2 + xH_2O$, where $x = 3$, 13 or 14 and $ZrBr(OH)_3 + yH_2O$ where $y = 1$ or 2. All of these compounds are deliquescent and decompose on exposure to moist air, the clear white crystals, often colored pink by free bromine present, melting to a gum, frequently with the evolution of hydrobromic acid. The salts are unstable even in dry air as was found on exposing dried crystals upon a watch-glass in a desiccator containing sulphuric acid. Much hydrobromic acid was evolved in the decomposition.

The crystals were prepared in two ways: either by dissolving pure $Zr(OH)_4$ in dilute hydrobromic acid evaporating upon a water-bath with subsequent additions of forty-eight per cent. hydrobromic acid and repeated evaporation, or a concentrated solution of hydrobromic acid was saturated with $Zr(OH)_4$, evaporated, and the crystals obtained on cooling.

As a rule the crystals obtained were quite soluble in the hot acid but separated at once on cooling. In the heating necessary for the thorough saturation of the hydrobromic acid by the $Zr(OH)_4$, the solution first becomes straw-colored then a deeper red, depending upon the time of the heating. This is evidently due to bromine from the decomposition of some hydrobromic acid.

A difficult problem was the removal of the strong hydrobromic acid mother-liquor and the free bromine nearly always present with the crystals. Of the methods tried to effect this, none proved satisfactory. The crystalline mass in one case was six times washed with ether, the yellowish-red solution, due to dissolved bromine, being decanted. Filtering proved too slow, permitting a rather long exposure of the crystals to the moisture of the air. After this washing with ether the crystals, still slightly yellow colored, were placed in a vacuum desiccator for the removal of the remaining ether. The small glass dish containing the material was allowed to remain thirty-six hours

in the vacuum desiccator. The substance was then removed, dried between filter-paper, and analyzed.

	Calculated for $ZrOBr_2.13H_2O$.	Found. I.	II.	III.
ZrO_2	24.01	24.15	24.50	24.60
Br	31.93	....	32.29	....
Loss at 124° C. less HBr evolved	....	....	24.44	....

This substance gave evidence of decomposition after being placed in the weighing bottle.

Another method used for the removal of bromine was washing the colored crystals three times with strong (forty-eight per cent.) solution of hydrobromic acid. Most of the bromine was thus removed although the salt remained slightly yellow, possibly due to the remaining hydrobromic acid. An interruption of the work at this point required the salt in this state to be placed in a desiccator over sulphuric acid. It remained there for several days when the work was resumed. All moisture seemed to be removed and great volumes of hydrobromic acid were given off when the desiccator was opened. The substance had taken on a brownish-red color around the edges but the central portion was perfectly white. To remove the excess of acid the substance was washed quickly three times with small amounts of water. All of these salts are exceedingly soluble in water and the utmost care is necessary to avoid the entire re-solution of the substance. The wash-water was deeply colored by the bromine removed and the salt remained pinkish. It was dried on filter-paper and an analysis gave 24.54 per cent. zirconium dioxide.

This shows that the method of removing the bromine and hydrobromic acid and drying the crystals, did not materially alter their composition. Alcohol did not give satisfactory results.

The ether-washed crystals, after being allowed to stand in a glass-stoppered weighing bottle in the balance case for several weeks, showed evidence of absorbed moisture. They were dried again by pressure between folds of bibulous paper, but they could not in this way be brought back to the same state as before, as shown by the analysis :

	Calculated for $ZrOBr_2.14H_2O$.	Found.	Previously found.
ZrO_2	23.70	23.49	24.50 (av.)
Br	30.82	30.58	.....

About four grams of these crystals were dried in a glass-stoppered flask under a rapid stream of dry hydrobromic acid at a temperature varying between 100° and 120°. The average temperature was about 110°, and the drying lasted continuously through three and a half days. After cooling, perfectly dry air was drawn through the flask for a little over ten minutes. This was supposed to be but was not long enough as the analysis showed that all the free hydrobromic acid had not been removed. It requires at least thirty minutes for thorough removal. The substance dried down to a hard, white, crystalline solid which was quite soluble in water. The composition of this salt was as follows:

	Calculated for $ZrOBr_2.4H_2O$.	Found. I.	II.
ZrO_2	36.21	34.91	34.82
Br	47.30	50.05	....

It is evident that the assignment of such a formula is largely guess work, but the cost in time and materials was too great for us to repeat the experiment.

Another experiment was carried out as follows:

One hundred cc. of forty-eight per cent. hydrobromic acid solution were saturated with wet $Zr(OH)_4$ by continuous boiling. The solution was never perfectly clear until it was twice filtered through compact filter-paper doubly folded. The clear yellow solution was concentrated by evaporation on the water-bath. The more concentrated it became the redder it was; finally the color was so deep that it appeared almost black. This was due to decomposition of the hydrobromic acid.

After concentration the liquid was cooled and white crystals separated out. On allowing it to stand twenty-four hours, or always when made too concentrated by further evaporation, a red jelly separated on top of these crystals. In trying to wash this jelly from around the crystals, for it was very soluble in water, the crystals were also dissolved. The whole was therefore redissolved and after several attempts a set of prismatic needles one to two mm. in length separated free from the jelly. This jelly was not silicic acid as feared. The mother-liquor was poured off, the crystals quickly washed three times with small amounts of water, dried between filter-paper, and analyzed:

	Calculated for $ZrBr(OH)_3.2H_2O$.	Found. I.	II.
ZrO_2	35.23	34.90	34.34
Br	31.01	30.79	....

The solution was further evaporated and another crop of needle crystals similar to, but much smaller than, the above obtained. They were washed four times in cold water, dried to a powder between filter-paper and analyzed :

	Calculated for $ZrBr(OH)_3.H_2O$.	Found. I.	II.
ZrO_2	37.91	36.86	36.35
Br	33.33	32.49	....

An investigation of the gelatinous oxybromide of zirconium showed that it was a hydrogele. On dialysis the small amount of crystalline oxybromide present passed through the membrane. At the same time the gelatinous compound, if it may be so termed, slowly decomposed into zirconium hydroxide and hydrobromic acid, the latter gradually passing through the septum while the former remained behind.

III. ZIRCONIUM OXYIODIDES.

According to Melliss, zirconium oxyiodide is not formed by dissolving $Zr(OH)_4$ in hydriodic acid. Hinzberg[1] secured an oxyiodide by precipitating a solution of zirconium sulphate with barium iodide in equivalent amounts. The solution was evaporated over sulphuric acid and the crystals washed with carbon bisulphide. The analysis gave $ZrI(OH)_3.3H_2O$.

In our experiments we found that zirconium hydroxide, when precipitated cold, was soluble to a small extent in strong aqueous hydriodic acid or could be dissolved by passing hydrogen iodide into water in which the zirconium hydroxide was suspended. Evaporation of this solution over sulphuric acid or calcium chloride gave needle-like crystals strongly colored with iodine and very hygroscopic. Every attempt failed at getting these freed from excess of iodine and properly dried. Washing with ether or with carbon bisulphide was ineffective. A hydrogele was gotten by acting upon zirconium hydroxide with hydrogen iodide, which formed on drying a hard, horn-like, colored mass insoluble in water and acids. This contained :

[1] *Ann. Chem.* (Liebig), **239**, 253.

	Per cent.
Zr	32.14
I	27.88
H_2O (by difference)	28.64

It lost only 11.07 per cent. of its weight after three hours' heating at 100°-120°.

UNIVERSITY OF NORTH CAROLINA.

ATROPINE PERIODIDES AND IODOMERCURATES.

BY H. M. GORDIN AND A. B. PRESCOTT.[1]

Received March 12, 1898.

I. ATROPINE ENNEAIODIDE.

IT has been known for a long time that in solutions of atropine salts, as in those of the salts of most other alkaloids, a solution of iodine in potassium iodide gives an insoluble precipitate. The nature of this precipitate has so far as we know not been thoroughly investigated. Jörgensen[2] has obtained and described two periodides of atropine: a triiodide and a pentaiodide. Our experience has taught us that in aqueous solutions the capacity of atropine for combining with iodine varies very widely, and the quantities taken up seem to depend upon the concentration of the liquids and even the order of mixing them.

The highest number of iodine atoms which a molecule of atropine can combine with, seems to be nine; between this and the above-mentioned triiodide lie the other compounds of atropine with iodine which are formed in aqueous solution. The same is true when chloroform is used as a solvent. We reserve for a later date a report upon the exact conditions which are necessary for the formation of any particular periodide of atropine. For the present we wish to say that under the conditions described below we were able to obtain the enneaiodide of atropine, $C_{17}H_{23}NO_3.HI.I_8$, as the sole combination of all the alkaloid, and sufficiently stable.

These conditions are the following: The concentration of the aqueous solution of the atropine salt should not exceed five-tenths per cent.; that of the iodine solution must not exceed one

[1] In the work of Research Committee D, Section 2, Committee on Revision of the Pharmacopeia of the United States.

[2] *J. prakt. Chem.* [2], 3, 329.

per cent.; the latter has to be acidulated with some sulphuric or hydrochloric acid; the atropine solution must be added to the iodine solution and not *vice versa*, and this addition must take place in small portions at a time, shaking the mixture thoroughly after each addition. At first the liquid becomes very turbid and particles of iodine are seen to be floating upon its surface; on continued addition of the atropine solution and shaking, the iodine-colored turbidity disappears, a dark granular precipitate falls out, and the supernatant liquid becomes perfectly transparent but is still dark-colored. If the addition of the atropine be stopped at this stage, *i. e.*, while the supernatant liquid has a very dark red color, the composition of the precipitate will be found to be that of the enneaiodide $C_{17}H_{23}NO_3HI.I_8$.

Whether additional quantities of atropine will make the precipitate take up more atropine and become a lower periodide we shall try to determine by later experiments. On the other hand when the order is reversed and the iodine solution is added to the atropine solution, it is always a lower periodide that is formed; but whether on continued addition of the iodine the precipitate will take up more of it and become a higher periodide, we cannot say as yet.

The enneaiodide, obtained as described, being unstable while moist and when removed from its mother-liquor, the precipitate has to be collected quickly by means of a pump, washed a few times with cold water and dried first on porous plates and then in vacuum over sulphuric acid. As thus obtained it is a very dark brown almost black powder, quite permanent in dry air and has only a slight odor of iodine. It is very difficultly soluble in ether, chloroform, benzene, or carbon disulphide, but is soluble in alcohol, very freely when hot. In cold water it is insoluble; hot water decomposes it quickly; it is also decomposed by concentrated solutions of potassium iodide. At 90° C. it commences to give up iodine vapors and at 140° C. melts to a dark liquid.

To obtain it in crystalline form it is first washed with a little cold alcohol to remove traces of free iodine and then dissolved in warm alcohol. On cooling it crystallizes out in dark-green prisms and leaflets, having the same properties as the non-crystallized body.

In this enneaiodide one-ninth of the total iodine is firmly combined just as in normal hydriodides, while eight-ninths is easily removed by reducing agents, such as sulphur dioxide and sodium thiosulphate. The compound therefore may be considered an atropine hydriodide octaiodide.

The additive iodine we estimated volumetrically and the total iodine both gravimetrically and volumetrically.

To estimate the additive iodine a small quantity of the enneaiodide is dissolved in very little alcohol, an excess of a standardized solution of sodium thiosulphate added and the excess titrated back with a standard solution of iodine using starch as the indicator.

For total iodine the substance is covered with an excess of powdered metallic zinc and some water and then boiled gently for ten or fifteen minutes, taking care to prevent loss by spurting; the mixture is then thrown upon a filter, and the containing flask and the filter thoroughly washed with hot water. The iodine in the zinc iodide thus formed can either be estimated by precipitation with silver nitrate and nitric acid and weighing as silver iodide, or it is precipitated with an excess of a standardized solution of silver nitrate and the excess titrated back with a standard solution of ammonium thiocyanate, using ferric nitrate as indicator.

Having obtained the enneaiodide of atropine it was natural to suppose the existence of a heptaiodide, with probability of a complete series from the triiodide to the enneaiodide. And in fact in the course of our work we once obtained this heptaiodide. But our efforts to determine the exact conditions necessary for the formation of this body have so far not been successful.

The easiest way to obtain the periodides of atropine is to use chloroform as a solvent. On adding twenty grams atropine to a warm solution of thirty grams iodine in chloroform (500 cc.) the enneaiodide crystallizes out very soon in the shape of small, shining, dark green crystals. If these be removed by filtration, the mother-liquor will give several successive crops of the dark blue pentaiodide and at last a crop of the brownish-red triiodide.

II. ATROPINE MERCURIC IODIDES.

The periodides of atropine, like those of many other alkaloids,

easily give double salts with mercuric iodide, obtained on shaking the alcoholic solution of the periodide with mercury and gently warming the mixture. This double iodide of atropine and mercury can also be made by mixing theoretical quantities of atropine and iodine, adding a little alcohol and an excess of mercury, slightly warming, and shaking till the color of iodine disappears. If the higher periodides of atropine be used in the preparation of this double iodide of atropine and mercury there is always separation of mercurous iodide; but if theoretical quantities of atropine and iodide are used there is no separation of mercurous iodide. The formula of this double iodide of mercury and atropine, as shown by our analysis, seems to be $C_{17}H_{23}NO_3.HI.HgI_2$. It resembles in composition several other double iodides of alkaloids and mercury obtained by Groves[1] by a different method. But besides this double iodide we also obtained another having the composition $(Atrop.HI)_2.HgI_2$. It was made by treating a solution of the $Atrop.HI.HgI_2$ in diluted alcohol with an excess of potassium iodide. From the liquid obtained by shaking an alcoholic solution of atropine and iodine with mercury the monoatropine hydriodide mercuric iodide crystallizes out in shining yellow crystals, melting at 89° to 90° C., difficultly soluble in ether or chloroform, partly soluble in hot water, and very soluble in warm alcohol. The diatropine hydriodide mercuric iodide obtained as said above by the action of potassium iodide on the mono compound, crystallizes in perfectly white, silky needles, which on being dried assume a yellowish tint. They melt at 98° to 99° C., are very easily soluble in warm alcohol, and quite soluble in hot water.

The analysis for mercury and for iodine in these bodies can be made in different ways, but the best results are obtained by a modification of the method of Risse.[2] The mercury and the iodine are determined in two separate portions. For mercury the substance is dissolved in a little warm alcohol and a little water added; the solution is then acidulated with a few drops of dilute hydrochloric acid and saturated with hydrogen sulphide. The mercuric sulphide is then dried and weighed in the usual way. For the determination of iodine the substance is treated

[1] *Quart. J. of Chem. Soc.*, 11, 97.
[2] *Ann. Chem.* (Liebig), 107, 223.

with a hot solution of potassium hydroxide (1 : 10), diluted with water, filtered, and when completely cold neutralized with acetic acid. The iodine is now precipitated with silver nitrate and nitric acid and determined as silver iodide in the usual way.

In the following analyses the standard silver nitrate solution was made to correspond with one per cent. of iodine and the ammonium thiocyanate solution to correspond, cc. per cc., with the silver nitrate solution. The standard solution of iodine contained one per cent. of iodine and the sodium thiosulphate solution corresponded, cc. per cc., with the iodine solution.

Analysis of the Atropine Enneaiodide not Recrystallized : Volumetric estimation for total iodine, 0.15225 gram required 12.2 cc. of the silver nitrate solution.

For the iodine removed by reduction, 0.19255 gram required 13.7 cc. of the thiosulphate solution.

	Calculated for $C_{17}H_{23}NO_3.HI.I_8$.	Found.
Iodine by reduction	70.88	71.15
Total iodine	79.74	80.13

In the gravimetric estimation from 0.218 was obtained 0.3207 silver iodide.

	Calculated for $C_{17}H_{23}NO_3.HI.I_8$.	Found.
Total iodine	79.74	79.48

Analysis of the Atropine Enneaiodide Recrystallized from Alcohol : The methods employed were the same as with the non-recrystallized compound and the standard solutions of the same strength.

In the volumetric estimation of total iodine, 0.12685 gram required 10.1 cc. of the silver nitrate solution. For the iodine removed by reducing agents, 0.23105 gram required 16.4 cc. of the thiosulphate solution.

	Calculated for $C_{17}H_{24}NO_3.HI.I_8$.	Found.
Total iodine	79.74	79.62
Iodine by reduction	70.88	70.98

In the gravimetric estimation of total iodine, 0.2031 gram gave 0.30035 silver iodide.

	Calculated for $C_{17}H_{23}NO_3.HI.I_8$.	Found.
Total iodine	79.74	79.90

Analyses of the Double Salts of Atropine Hydriodide and Mercuric Iodide: 0.2632 gram of the monoatropine hydriodide mercuric iodide gave 0.0699 gram mercuric sulphide, and 0.30445 gram of the substance gave 0.24785 gram silver iodide.

	Calculated for Atrop. HI.HgI_2.	Found.
Mercury	23.03	22.89
Iodine	43.74	43.98

Of the diatropinehydriodide mercuric iodide, 0.1798 gram gave 0.032 gram mercuric sulphide, and 0.257 gram of the substance gave 0.18885 gram silver iodide.

	Calculated for $(Atrop.HI)_2.HgI_2$.	Found.
Mercury	15.58	15.34
Iodine	39.46	39.70

III. ATROPINE ESTIMATION AS PERIODIDE.

The formation of atropine enneaiodide under the conditions described above affords a convenient method for estimating the strength of atropine solutions by means of a standard solution of iodine and titrating back with a standard solution of sodium thiosulphate. The way to operate is as follows: The atropine solution, whose strength is approximately determined by a preliminary experiment, operating in the way described below, is diluted with water so as to contain at most four-tenths to five-tenths per cent. of the alkaloid and in so doing the solution is made up to a given volume. Twenty or thirty cc. of a decinormal iodine solution are now put into a measuring flask holding 100 cc., diluted with a little water, and acidulated with a few drops of diluted sulphuric acid; the atropine solution is now run in from a burette slowly, and in small portions at a time, shaking the flask thoroughly after each addition and observing whether the supernatant liquid commences to clear up. If not, a little more of the atropine solution is added, and the mixtures again shaken for a minute or two. In this way the addition of atropine is slowly continued till after a few shakings the supernatant liquid commences to become transparent, still having a dark red color, which can easily be seen by stoppering the flask, reversing it and looking through its neck. The addition of atropine is then stopped, the flask shaken till the supernatant liquid

is perfectly transparent, and then it is diluted to 100 cc. Of this liquid an aliquot portion is filtered off and the excess of iodine in it determined by a decinormal solution of sodium thiosulphate. Every part by weight of iodine consumed corresponds to 0.2849 part of alkaloid or every cubic centimeter of the decinormal iodine solution consumed corresponds to 0.0036048 gram of atropine alkaloid.

These factors are obtained on the ground that for the formation of the atropine enneaiodide only eight atoms of iodine are supplied by the free iodine used to make the decinormal iodine solution, the ninth atom coming from the potassium iodide of that solution. The success of this method depends solely upon the atropine solution being sufficiently diluted, as otherwise a resinous mass is liable to be formed instead of a granular precipitate, and added in small portions at a time to the iodine solution, care being taken to shake the mixture after each addition and to stop the operation as soon as the supernatant liquid commences to become transparent, being still red-colored. It is easy to be guided by the very dark color, as an excess of atropine makes the liquid almost colorless. With a little care the method gives very good results, as can be seen from the following analyses.

Whether this method of assay is applicable to the crude drugs containing atropine and their galenical preparations, we shall try to determine by experiments to be continued.

In conclusion we wish to say that the method of using a solution of iodine and potassium iodide for the quantitative estimation of alkaloids has been long since proposed,[1] and recently Kippenberger[2] has given considerable prominence to this method in his toxicological and other researches. But he rests upon the assumption of the formation of the atropine triiodide, and this may be the leading product under the particular conditions he prescribes; but his method as a whole, when tried in this laboratory, has not given satisfactory results. The estimation of caffein as a periodide recently published by Gomberg[3] proves highly satisfactory.

[1] Bouchard: *Compt. rend.*, 9, 475; R. Wagner: *Ding. poly. J.*, 161, 40; *Ztschr. anal. Chem.*, 1, 102.

[2] *Ztschr. anal. Chem.*, 35, 10; 34, 317, etc.

[3] This Journal, 18, 331.

In the following estimation of the strength of atropine solutions both the iodine solution and the sodium thiosulphate solution were strictly decinormal. Of the iodine solution twenty or twenty-five cc. were put into a 100-cc. measuring flask and atropine solutions of known strength run in from a burette and the operation continued as described above. When the supernatant liquid was perfectly transparent the flask was filled up to 100 cc. and fifty cc. were filtered off. In these fifty cc. the excess of iodine was determined by means of the tenth-normal thiosulphate solution and the strength of the atropine solutions calculated by using the factor 0.0036048 for every cubic centimeter of decinormal iodine used up.

No. of sample.	Number of cc. of the atropine solution taken.	Number of cc. of the tenth-normal iodine used up.	Calculated strength. Per cent.	Actual strength. Per cent.
1	12	15.6	0.47	0.50
2	15	14.9	0.36	0.40
3	17	13.2	0.28	0.30
4	12	10.0	0.28	0.25

We shall try to determine experimentally whether this method is also applicable to other alkaloids and their galenical forms.

The above-mentioned factor for every cubic centimeter of the decinormal iodine solution was deduced as we said upon the ground that only eight atoms of iodine of every molecule of the atropine enneaiodide are furnished by the free iodine of the iodine solution—the ninth atom forming the normal iodine of the enneaiodide coming from the potassium iodide.

That this is really so has been admitted by almost all chemists in the case of all other periodides whose constitution is similar to that of the atropine enneaiodide. It would, therefore, seem to be superfluous to prove experimentally the correctness of this view with regard to the enneaiodide of atropine. But owing to the fact that Kippenberger in the above-cited articles advances a different view we thought it advisable to prove irrefutably that the iodide of potassium of the iodide solution takes an active part in the reaction by which the atropine enneaiodide is formed and gives off an amount of iodine which is just equal to the amount of the normal iodine of the enneaiodide.

We proceeded in the following manner: We first determined the strength of our iodine solution with regard to free iodine;

this was done by means of a sodium thiosulphate solution of known strength. We then took ten cc. of this iodine solution and determined the total amount of iodine, free as well as bound to potassium, by shaking them in a flask with an excess of powdered metallic zinc till the color of iodine disappeared, filtering the solution of zinc iodide and potassium iodide thus obtained, washing the flask and the excess of zinc with hot water and precipitating the iodides in the filtrate with silver nitrate and nitric acid. From the weight of silver iodide, washed and dried in the usual way, we calculated the amount of total iodine present in our iodine solution. By subtracting the amount of free iodine from that of the total iodine we obtained the amount of iodine present in our solution as potassium iodide. We thus found that the iodine solution contained one per cent. free iodine and 1.2312 per cent. combined iodine.

We then put forty cc. of this iodine solution in a 100-cc. measuring flask, added twenty cc. of a three-tenths per cent. solution of atropine alkaloid, and, after shaking well, diluted the liquid in the flask to 100 cc. We now took two vials and in each filtered off twenty-five cc. from the flask. In the first vial the amount of free iodine titrated back with sodium thiosulphate was found to be 0.0465. From this it is easy to deduce that the twenty cc. of the three-tenths per cent. atropine solution consumed 0.214 gram of the free iodine. In the second vial the total iodine was determined in the same way as described above and the quantity of silver iodide was found to be 0.3023 gram which shows that after the treatment with atropine the liquid contained 1.633 per cent. total iodine. From these data we deduce that the twenty cc. of the atropine solution have taken up 0.02528 gram iodine from the bound iodine. As the twenty cc. of atropine solution contained 0.06 gram atropine we find for 100 parts of precipitated enneaiodide

	Found. Per cent.	Calculated. Per cent.
Atropine	20.05	20.26
Iodine taken from the free iodine of the iodine solution.....	71.50	70.88
Iodine from the iodine bound as KI..	8.45	8.86

We see that in aqueous acidulous solutions the potassium iodide takes an active part in the reaction by joining in a yield of hy-

driodic acid for the normal hydriodide of the alkaloid, necessary to hold the additive iodine of the periodide. When carbon disulphide or carbon tetrachloride is used as solvent for the atropine and the iodine, no periodide seems to be formed, possibly for the reason of there being no generation of hydriodic acid for the making of hydriodide. As to the formation of the periodides in chloroformic solutions of atropine and iodine, it might possibly be explained by the substituting action of iodine either upon the chloroform or upon a side-chain of the atropine.

The direct substitution of iodine for some of the hydrogen in these bodies might, in this case, be made possible by the presence of the natural base which combines with the hydriodic acid, when formed by such a substitution. Part of the atropine would then act in a manner similar to that of mercuric oxide, which is usually employed in the iodizing of hydrocarbons. An analogous case we have in the easy substitution of iodine for some of the hydrogen in aniline, a part of which combines with the hydriodic acid, which is set free through the substitution of iodine for hydrogen in another part. At any rate we shall endeavor to determine the by-products formed when atropine enneaiodide is produced in chloroformic solutions.

UNIVERSITY OF MICHIGAN,
FEBRUARY 28, 1898.

COMPOSITION OF THE ASHES OF SOME RAW TANNING MATERIALS.[1]

BY WM. K. ALSOP AND J. H. YOCUM.

Received March 15, 1898.

NO systematic investigation of tannin sources has been published which covers not only the tannin itself, but also the other chemical compounds found in the raw material. With the object of making a complete analysis of some of the common sources of tannin, we present this paper on the ash and tannin analysis, and hope in the future to present others bearing upon the sugars and other soluble non-tannins, celluloses, and red coloring material.

In the table presented showing the tannin content of oak and hemlock bark, the averages from two widely separated localities for each of a large number of analyses, are given. The method

[1] Read before the New York Section, March 11, 1898.

of determining the tannin followed, was that of the Association of Official Agricultural Chemists for 1897. The total extract is the result obtained by extracting the bark with boiling water and evaporating the solution; the residue left in the extractor is reported as cellulose and insoluble, and was obtained by difference. A larger total extract can be obtained if alcohol be used as the extracting medium, this increase being of the nature of the red coloring material, hence the residue from a water extraction is not pure cellulose. The total extract (with water) when at 95° C., dissolves a considerable portion of the red coloring material from the bark, they being precipitated upon cooling the solution. The soluble solids are the solids of extract solution soluble at 18° C., and the red coloring material is the difference between total solids and soluble solids. The non-tannins are that portion of the soluble solids not absorbed by hide and are mainly glucosides of unknown composition. Tannins are the difference between soluble solids and non-tannins. Moisture was determined by drying at 100° C. In the table giving the ash analysis, the results, marked $Al_2O_3 + Fe_2O_3$, represent practically alumina, as only traces of ferric oxide could be found in the precipitate.

The extract results give the portion of the ash removed by leaching, since it required three portions of bark to make one of extract. During the extraction only 0.44 per cent. of ash was removed from the bark. The very much greater ash of oak over hemlock bark and the higher proportionate amount of lime is no doubt due to the fact that hemlock does not grow on a limestone soil.

	Chestnut-oak bark.	Chestnut-oak bark.	Hemlock bark.	Hemlock bark.	Quebracho wood.	Oak-bark extract.
Number of samples	118	117	81	50	1	1
Total extract	24.69	19.76	19.33	19.96	24.80	46.92
Total soluble solids	20.36	16.26	15.40	16.11	19.20	45.96
Red coloring material	4.33	3.50	3.93	3.85	5.60	0.96
Non-tannins	9.81	8.21	6.74	6.44	3.64	20.29
Tannins	10.55	8.05	8.66	9.67	15.56	25.67
Moisture	10.85	9.73	11.57	13.75	11.60	53.17
Cellulose and insoluble matter	64.46	70.51	69.10	66.29	63.60	....

	Chestnut-oak bark. No. 1.	Chestnut-oak bark. No. 2.	Hemlock bark. No. 3.	Hemlock bark. No. 4.	Quebracho wood. No. 5.	Oak-bark extract. No. 6.	Leached oak bark. No. 1.	Leached oak bark. No. 2.	Leached hemlock bark. No. 3.
Ash	6.02	8.05	1.65	1.45	0.88	1.35	6.35	6.96	1.55
Carbon	0.77	0.11	0.23	0.59	0.11	1.57	0.15	0.15	....
Sand and silicic acid	2.34	3.33	....	....	0.88	1.88	....	....	7.15
Sand	....	....	1.12	3.53	....	....	1.52	1.46	....
SiO_2	....	...	0.78	2.84	....	....	1.40	0.77	....
$Al_2O_3+Fe_2O_3$	0.08	0.86	3.07	3.86	0.64	5.59	0.71	0.55	2.05
MnO	1.26	0.33	2.26	4.09	0.10	2.21	0.58	0.28	2.41
CaO	52.63	58.24	52.52	49.35	61.27	19.15	57.42	60.50	53.97
MgO	1.18	1.77	1.98	2.92	4.56	2.38	0.56	1.13	1.68
K_2O	2.95	2.62	6.02	7.64	0.24	29.44	1.77	0.84	2.35
Na_2O	0.63	0.40	0.27	0.95	1.22	1.01	0.44	0.38	0.66
Cl	0.44	0.10	0.20	0.24	not det	not det	0.10	0.19	not det
SO_3	0.17	0.12	0.82	1.88	1.11	2.86	0.17	0.12	1.71
P_2O_5	0.64	1.13	2.62	2.94	0.50	3.72	0.51	0.15	1.98
CO_2	36.51	31.47	27.66	19.10	28.30	not det	33.88	33.15	25.50
	99.60	100.49	99.55	99.93	98.93		99.21	99.67	99.46

[CONTRIBUTIONS FROM THE CHEMICAL DIVISION OF THE U. S. DEPARTMENT OF AGRICULTURE, No. 33.]

ON THE DETERMINATION OF POTASH WITHOUT THE PREVIOUS REMOVAL OF IRON, CALCIUM, ETC.

BY C. C. MOORE.[1]

Received March 18, 1898.

I HAVE found it practicable to wash out ferric, aluminic and other chlorides, and the excess of platinic chloride which is present by means of an acidulated alcoholic wash. Thus it is possible to avoid the precipitation and filtering of ferric hydroxide, calcium oxalate, etc., and the subsequent evaporation and ignition for the removal of ammoniacal salts.

The substance under examination is brought into solution by the usual acid digestion, and the excess of acid removed by evaporation, the residue and insoluble matters separated by filtration. The filtrate is now ready for the potash estimation. To it is added the usual platinic chloride solution, only enough

[1] Communicated by Dr. H. W. Wiley.

to combine with the potash being necessary. The mixture is evaporated, on the steam-bath, nearly to dryness, so that it solidifies on cooling, just as in the ordinary determination. From fifteen to twenty-five cc. of the acidulated alcohol are added, and allowed to stand two or three minutes with an occasional stirring. The ferric, aluminic, etc., and excess of platinic chlorides readily go into solution, leaving the crystallized potassium chlorplatinic salt and part of the neutral sulphates, sodium chloride, etc. These residues are brought onto a filter, either paper or Gooch, and after one or two washings by decantation, the potassium chlorplatinate and the other residue are washed onto the filter, and washing continued with the same acidulated alcohol until all excess of platinic chloride is washed out. Now wash with the Lindo ammonium chloride solution (200 grams ammonium chloride to one liter of water) until sulphates, sodium chloride, etc., are washed out. Then wash out the ammonium chloride with eighty-five per cent. alcohol, after which a pure potassium chlorplatinate salt is left, which is dried and weighed as usual.

The acidulated alcohol is prepared by passing dry hydrochloric acid gas into cool ninety per cent. alcohol. This is easily done by gently heating strong aqueous hydrochloric acid in a flask. The liberated gas is passed through sulphuric acid, and into the alcohol which is kept in a cooled vessel. Some ethyl chloride will be formed, but most of the gas will be held in solution mechanically by the alcohol. The absorption is continued until one cc. of the alcohol neutralizes about two and one-third cc. of a normal potassium hydroxide solution, using phenolphthalein or any other suitable indicator.

The solvent action of this acidulated alcohol on potassium chlorplatinate is about equal to that of the Lindo ammonium chloride solution, and about one-third that of ordinary eighty per cent. alcohol. Or, if expressed in figures, one gram of pulverized potassium chlorplatinate was digested for two hours in 500 cc. of acidulated alcohol, at a room temperature of 80°, the flask being shaken continuously. The solvent action under these conditions was found to be one part in 60,000.

In experimenting, the ash sample used by the "Association of Official Agricultural Chemists" in 1897 was used. The reporter

found this ash to contain about 11.05 per cent. of potash. The sample was digested in hydrochloric acid, evaporated to dryness and taken up with hydrochloric acid and water, so that the portion of the filtrate used corresponded to one-half gram of ash, and contained less than one-half cc. of hydrochloric acid. Four portions were taken from each of two samples, and only sufficient platinic chloride was added to combine with the potassium chloride present. The variation of the maximum and minimum results in each sample was 0.03 per cent., and the average of the eight determinations varied 0.01 per cent. from the result found by the Association.

It was desired to see under what extreme conditions the potash could be determined. An aliquot portion corresponding to one-half gram was used. To this were added 2.0 grams ferric chloride, 0.30 gram aluminic chloride, 0.20 gram sodium chloride, and 0.03 gram calcium sulphate, and only sufficient platinic chloride to combine with the potassium chloride. The result was less than 0.40 per cent. higher than the known percentage, and it is possible that potash was in the chemicals added.

Again, a solution was made of 0.30 gram potassium chloride, 0.56 gram calcium sulphate, 1.00 gram sodium chloride, and 7.0 grams ferric chloride. Only five cc. of a standard solution of platinic chloride were added, which is but a trifle above the requisite amount for the potassium chloride. Duplicate determinations and a blank were run. The evaporation was continued until a solution of the consistency of molasses was formed amounting to about five cc. To wash each sample in a Gooch, 190 cc. of the acidulated alcohol, and 250 cc. of ammonium chloride solution were used, and thirty-five minutes required for complete washing.

While one sample recovered 110 per cent. of the original potassium chloride, the second result was 100.50 per cent., and the blank was not stained. The potassium chlorplatinate crystals were below medium size, very uniform and of splendid color.

It was observed that the presence of other salts was beneficial, as it made the crystallization of the potassium chlorplatinate more perfect, and prevented any subsequent reduction.

Should the original substance contain ammoniacal salts, they

must be removed, else ammonium chlorplatinate will be formed.

The decomposition and removal of ammoniacal salts by nitric acid is most applicable here. The process is described in "Crookes' Select Methods," page 32. If hydrochloric acid is present, it is beneficial, as the chlorine which would be liberated also decomposes ammoniacal salts.

THE DETERMINATION OF METHANE, CARBON MONOXIDE, AND HYDROGEN BY EXPLOSION IN TECHNICAL GAS ANALYSIS.

By W. A. Noyes and J. W. Shepherd.

Received March 7, 1898.

THE determination of carbon monoxide in technical gas analysis with the Orsat apparatus is not very satisfactory, partly because the gas is absorbed so slowly by the cuprous chloride, and partly because the cuprous chloride must be very frequently changed unless two absorption bulbs filled with the reagent are used. These difficulties may be avoided and the carbon monoxide, hydrogen, methane, and nitrogen may be determined by explosion, if the determination is accompanied by a determination of the oxygen consumed in the combustion, by explosion, of a known volume of the gas. For this purpose we have introduced in the Orsat apparatus in place of the fourth bulb an explosion pipette of the form shown in Fig. 1. The pipette has the advantage over that usually supplied with apparatus for gas analysis, that during the explosion the gas is confined by glass stop-cocks on both sides, insuring positively against loss during the moment of high pressure in the apparatus. A little sulphuric acid is added both to the water in the explosion pipette and to that in the measuring burette. This greatly decreases the ionization of the carbonic acid and so lessens the solubility of the carbon dioxide in the water. The results given below demonstrate that the error arising from the solubility of carbon dioxide in dilute acid in the case of mixtures containing six to eight per cent. of the gas must be very small.

Fig. 1.

For the purpose of determining the amount of oxygen remaining after the explosion, we have attached to the outer end of the capillary tube of the Orsat apparatus a small hydrogen generator of the form shown in Fig. 2. The hydrogen is generated from aluminum foil and a solution of potassium hydroxide of sp. gr. 1.27. The lower bulb of the generator should have a capacity of about twenty cc. The stopper bearing the delivery-tube of the generator is pushed into its mouth and covered with water to avoid diffusion of the hydrogen, and the rubber connection with the capillary tube of the Orsat is surrounded with a glass tube filled with water for the same reason. With these precautions, hydrogen, which is almost chemically pure, may be taken into the measuring tube of the apparatus whenever desired.

Fig. 2.

The analysis is carried out as follows: In the case of illuminating gas the carbon dioxide is absorbed in potassium hydroxide of sp. gr. 1.27, the illuminants in fuming sulphuric acid followed by the caustic potash, and the oxygen in an alkaline solution of pyrogallol. The residue is then left over the pyrogallol, the side bottle is raised till all gas is expelled from the capillary tube of the apparatus, and then about eighty-five cc. of air are taken in and accurately measured. In all measurements three minutes were allowed for the water to run down the walls of the burette. The burette was kept at a constant temperature by running water through the jacket surrounding it, as the temperature of the room where we worked was quite variable. To facilitate accurate reading, a scale corresponding to the scale of the burette, was made on the edge of the case of the apparatus. By means of such a scale it is very easy to bring the water in the side bottle to the level of the water in the measuring tube and also to bring the eye to the exact level required. After measuring the air, gas is admitted from the residue over the pyrogallol. The amount to be taken will vary, of course, with its character. It should be taken in such amount as to require nine to ten cc.

of oxygen for its complete combustion. If too much is taken, there may be danger of burning nitrogen, and also there will not be enough oxygen left for the second explosion with hydrogen. With a gas of unknown composition six to eight cc. may usually be taken at first and, if the mixture will not explode, hydrogen may be added, one cc. at a time, till an explosion can be secured. From the data thus secured the amount of the gas which should be used can be determined. Before attempting an explosion the gas should be passed into an explosion pipette and back to the measuring burette at least twice, and better three times, to secure thorough mixing. After the explosion the contraction is determined and then the carbon dioxide. Then about twenty cc. of hydrogen are added, and after mixture as before, and explosion, the contraction is determined. One-third of this contraction will give the amount of oxygen remaining after the first explosion. If this amount of oxygen be subtracted from the amount in the air originally taken, the difference will be the amount of oxygen used in the first explosion. Air is assumed to contain 20.9 per cent. of oxygen in these calculations.

The calculation of the results is based on the following equations, in which the symbols are used to represent volumes of gas:

1. $CH_4 + CO + H + N =$ Gas taken.
2. $2CH_4 + \frac{1}{2}CO + \frac{3}{2}H =$ Contraction.
3. $2CH_4 + \frac{1}{2}CO + \frac{1}{2}H =$ Oxygen consumed.
4. $CH_4 + CO = CO_2$ formed.

Hence

$H =$ Contraction less oxygen consumed.

$CO = \frac{2}{3}(2CO_2 + \frac{1}{2}H - O$ consumed).

$CH_4 = CO_2 - CO.$

$N =$ Total gas $- (H + CO + CH_4).$

The following is an illustration of the record of an analysis:

	Reading.	Volume.
Air	12.96	87.04
Gas	0.58	12.38
Contraction	15.4	14.82
CO_2	23.39	7.99
H	1.24	22.15
Contraction	24.35	23.11
Oxygen originally present	....	18.19
" of second explosion	....	7.71
" of first explosion	....	10.48

Hence

		Per cent.
Hydrogen	= 4.34	= 35.06
Carbon monoxide	= 5.12	= 41.38
Methane	= 2.87	= 23.19
	12.33	99.63

To determine the accuracy of the method, a mixture of known composition was prepared. Hydrogen was first admitted into the measuring tube of the burette, from the generator described, and then methane, generated from sodium acetate and soda-lime, was introduced. After thorough mixture, three determinations of the proportion between the methane and hydrogen were made in the usual manner by explosion. The results agreed quite closely with the composition of the gas as determined by measurement, indicating that the methane was practically pure.[1] The results were :

	Calculated.	Found.			Average.
Methane	38.5	39.9	39.3	39.2	39.5
Hydrogen	61.5	60.0	60.0	60.7	60.2
	100.00	99.9	99.3	99.7	99.7

	Calculated.	Found.			Average.
Methane	37.6	38.2	38.0	38.5	38.2
Hydrogen	62.4	60.9	61.3	60.2	60.8
	100.00	99.1	99.3	98.7	99.0

There seems to be some tendency to high results for methane, but the close approximation to 100 for the total indicates that there was probably some loss of hydrogen by diffusion or absorption. If the gases are thoroughly mixed before explosion, there would seem to be no occasion for such gross errors in the determination of hydrogen as were observed by Gill and Hunt.[2] Gases mix by diffusion very much less quickly than is commonly supposed.

The remainder of the mixture of methane and hydrogen was then carefully measured and a mixture of carbon monoxide and carbon dioxide obtained by heating oxalic acid with concen-

[1] This accords with the statement of Freyer and Meyer, *Zeit. phys. Chem.*, 11, 28, but not with that of Gill and Hunt in this Journal, 17, 968.

[2] This Journal, 17, 992.

trated sulphuric acid was added. After removal of the carbon dioxide, the gas was again measured, and, on the basis of the result, combined with the results of the analysis of methane and hydrogen, the composition of the total gas was calculated. A series of analyses of the mixture was then made.

FIRST SERIES.

	Calculated.	Found.					Average
Methane	23.08	23.6	23.0	22.8	23.3	23.3	23.21
Carbon monoxide	41.52	39.6	40.6	40.9	41.2	40.5	40.55
Hydrogen	35.23	35.0	35.6	35.4	35.0	34.5	35.09
	99.83	98.2	99.2	99.1	99.5	98.3	98.85

SECOND SERIES.

	Calculated.	Found.						Average
Methane	22.37	22.7	23.1	22.6	22.7	22.7	22.4	22.68
Carbon monoxide	41.48	40.4	40.0	40.5	40.2	39.8	40.0	40.15
Hydrogen	35.80	35.3	35.4	35.6	35.9	35.7	35.9	35.64
	99.65	98.4	98.5	98.7	98.8	98.2	98.3	98.47

The objection that the error is multiplied because of the small amount of gas which must be taken for the explosion, applies to this method as it does to the usual explosion method for methane and hydrogen, of course. It is to be noticed, however, that the determination of methane, the most valuable constituent as a fuel, depends on the combined measurements of the carbon dioxide, the contraction, and the oxygen consumed, instead of depending on the carbon dioxide alone, as is the case with the older method. By the method in common use any carbon monoxide which has failed of absorption is counted as methane after the explosion. Another advantage is that the errors are of a compensating nature, so that when methane is found too high, carbon monoxide and hydrogen will usually be found low, and in such ratio that the total fuel value will be nearly constant.

We have used with the Orsat apparatus a stop-cock lubricant described by Professor Ramsay at the Toronto meeting of the British Association, though he said it was not original with him. Equal parts of black rubber, vaseline, and paraffin are heated to gentle boiling for a quarter of an hour in a beaker. The lubricant is sufficiently viscous to hold against an atmosphere of pressure, if necessary, gives no hydrocarbon vapor to a vacuum, and

the stop-cocks in which it is used do not become set even after long standing. The last property makes it especially valuable for the Orsat apparatus.

ROSE POLYTECHNIC INSTITUTE.

PROTEIDS OF THE PEA.[1]

BY THOMAS B. OSBORNE AND GEORGE F. CAMPBELL.

Received March 29, 1898.

IN a paper on the "Proteids of the Pea and Vetch"[2] the legumin obtained from these seeds was described and some account was also given of other accompanying proteids. Further study has furnished much additional information concerning these substances and made necessary a review of our former work on the pea and vetch.

On investigating the proteid constituents of the horse bean and lentil we found that by repeated fractional precipitations, the globulin from these seeds was separated into fractions, on the one hand wholly free from coagulable matter and on the other consisting of substance which was substantially all coagulable. The former we found to be legumin, in all respects like that described by us from the vetch, and the latter to be a new proteid of different composition and properties, to which we have given the name *vicilin* since we first recognized its presence in the horse bean (*vicia faba*).

This discovery led us to reinvestigate the proteids of the pea and we thus found that the legumin of that seed, as formerly described by us, was contaminated with more or less vicilin and that when the latter is completely separated the differences noted in our former paper between the legumin of the pea and that of the vetch disappear and preparations from these two seeds are identical in composition and reactions.

Leguminous seeds contain about one and two-tenths per cent. of alkali and one per cent. of phosphoric acid, while in the seeds of the cereals but five-tenths and seven-tenths per cent. of these substances respectively are present.

Liebig and Rochleder as well as Ritthausen attributed the

[1] Reprinted from advance sheets of the report of the Connecticut Agricultural Experiment Station for 1897. Communicated by the authors.

[2] This Journal, 18, 583; Report of the Connecticut Agricultural Experiment Station for 1895.

presence of much legumin in the aqueous extracts of leguminous seeds to the basic alkali phosphates. But the water extracts are strongly acid to litmus and accordingly must contain acid phosphates.

We find that a mixture of hydrogen potassium phosphate with enough phosphoric acid to be distinctly acid to litmus, but strongly alkaline to lacmoid, freely dissolves legumin to solutions that behave in all respects like the aqueous extracts of these seeds. Such solutions are unlike those obtained with neutral salts, not being easily precipitated by dilution unless holding a very large proportion of proteid. They yield precipitates with acetic acid which are wholly soluble in sodium chloride brine, thus resembling solutions in sodium bicarbonate.

In this and the following papers we give the results of our investigation upon each seed, and in the last paper, a general summary of the properties and composition of the different proteids which we have found.

Finely ground meal of garden peas was prepared in the laboratory almost entirely free from the outer coating of the seed. Immediately after grinding, 1,800 grams were treated with a large quantity of ten per cent. salt solution, strained through fine bolting-cloth and, after standing three hours to deposit insoluble matter, the turbid extract was siphoned off and saturated with ammonium sulphate. The precipitate was filtered out, suspended in a little water and dialyzed for eighteen hours. A large part of the ammonium sulphate was thus removed and the proteid dissolved by the dilute saline solution which remained. This solution was filtered perfectly clear through a thick felt of paper pulp and dialyzed for four days. A large precipitate resulted from which, after settling, the solution, A was decanted and treated as described on page 353 ; the precipitate was dissolved in about 1500 cc. of ten per cent. brine, the solution filtered clear and made exactly neutral to litmus paper by the cautious addition of seventy-five cc. of two-tenths per cent. potash water. The solution was then dialyzed for forty hours, whereby globulin separated out in well-defined spheroids which, after settling, united to a coherent mass exactly like vetch legumin, and differing from our previously described pea legumin that had formerly been obtained as a pulverulent pre-

cipitate. A portion of this precipitate was washed thoroughly with water and with alcohol and dried over sulphuric acid, giving 16.83 grams of preparation 32, which had, after drying at 110°, the following composition:

GLOBULIN, 32.[1]

Carbon	51.87
Hydrogen	7.01
Nitrogen	17.69
Sulphur	0.40
Oxygen	23.03
	100.00
Ash	0.62

This preparation, unlike those made from unneutralized solutions, was almost free from substances insoluble in salt solution. Dissolved in ten per cent. brine and heated above 90°, turbidity was produced, which at 98°–100° developed slowly into a considerable coagulum.

During the washing of this preparation considerable substance dissolved in water, yielding a solution which was perfectly neutral to litmus (indicating the absence of acid globulin), and which on adding a little salt, gave a precipitate that with more salt dissolved completely to a solution coagulable by heating.

The remainder of the proteid, of which 32 was a part, was dissolved by adding fifty cc. of ten per cent. salt solution and the resulting liquid was diluted with water until it contained about 1.25 per cent. of salt. A large part of the proteid was thus thrown down and settled out as a viscid layer, from which after an hour the supernatant fluid was almost completely decanted. This deposit, X, was then washed with 200 cc. of water, which caused it to become opaque and pasty. The wash-water, after decanting, was added to the solution from which the proteid had separated, and thereupon another precipitate, Y, resulted, from which, after settling, the solution was decanted and dialyzed, thereby yielding precipitate Z.

As precipitate X was found to give a decided turbidity on heating its solution in a boiling water-bath, it was dissolved by add-

[1] To avoid confusion and facilitate reference the preparations described in this paper are numbered consecutively with those given in the paper on "Legumin and other Proteids of the Pea and Vetch," this Journal, 18, 583.

ing ten grams of sodium chloride and water enough to make a final volume of 350 cc. The clear solution which resulted, containing about three per cent. of salt, was diluted with water until it contained about one and three-fourths per cent. of salt. A large precipitate, I, separated, which rapidly settled as a viscid, semi-fluid layer from which the solution II was soon completely decanted. As the precipitate I, when dissolved in salt solution, still gave a slight turbidity on heating to 99°, it was washed with water, dissolved in 100 cc. of ten per cent. salt solution, and reprecipitated by diluting the resulting clear liquid with 900 cc. of water. The precipitate which separated was now found to be wholly free from any coagulable matter, for not the slightest turbidity was produced in its solutions in brine even by prolonged heating in a boiling water-bath. The substance was therefore washed thoroughly with water and with alcohol and dried over sulphuric acid, thus giving 12.33 grams of preparation 33, which had, when dried at 110°, the following composition:

LEGUMIN, 33.

Carbon	51.74
Hydrogen	6.90
Nitrogen	18.04
Sulphur	0.42
Oxygen	22.90
	100.00
Ash	0.78

The solution decanted from 33 was dialyzed free from chlorides and a precipitate obtained which when washed and dried in the usual manner weighed 4.44 grams and had the composition shown by the following figures:

GLOBULIN, 34.

Carbon	52.06
Hydrogen	6.99
Nitrogen	17.86
Sulphur	0.36
Oxygen	22.73
	100.00
Ash	0.32

Solution II, page 351, was next diluted with an equal volume of water until it contained about nine-tenths per cent. of salt; after standing a short time the solution was decanted and the liquid precipitate washed thoroughly with water and alcohol and dried, giving 6.47 grams of preparation 35.

GLOBULIN, 35.

Carbon	51.95
Hydrogen	6.96
Nitrogen	17.76
Sulphur	0.42
Oxygen	22.91
	100.00
Ash	0.57

The filtrate from 35 was dialyzed free from chlorides and yielded 5.18 grams of preparation 36, which after the usual treatment gave on analysis the following results:

GLOBULIN, 36.

Carbon	52.43
Hydrogen	7.04
Nitrogen	17.45
Sulphur	0.23
Oxygen	22.85
	100.00
Ash	0.40

Preparations Y and Z obtained as successive precipitates from the solution decanted from X, as described on page 350, were separately washed with water and alcohol and dried over sulphuric acid, giving respectively preparation 37, weighing 8.06 grams, and preparation 38, weighing 6.80 grams. These had the composition given below:

GLOBULIN.

	37	38
Carbon	52.08	52.20
Hydrogen	6.90	7.01
Nitrogen	17.65	17.53
Sulphur	0.28	0.15
Oxygen	23.09	23.11
	100.00	100.00
Ash	0.75	0.46

The solution, described on page 349, that had been decanted from the mixed globulin and after forty hours' dialysis had yielded the preparations 32–38, was further dialyzed for four days and 11.2 grams of globulin obtained having, when dried at 110°, the following composition:

GLOBULIN, 39.

Carbon	52.45
Hydrogen	7.04
Nitrogen	17.22
Sulphur	0.16
Oxygen	23.13
	100.00
Ash	0.18

It will be noticed that by this extensive fractional precipitation of the pea globulin, a separation was effected which yielded legumin, agreeing in reactions with that of the vetch as formerly described, and with that of the lentil and horse bean, as will be shown later in this paper, and vicilin, a more soluble globulin of somewhat different composition, which is coagulated by heating its solutions to about 95° and has a very remarkably low content of sulphur. The composition of vicilin is shown by the analyses 36, 38 and 39, which represent the most soluble globulin contained in the solutions from which they were separated.

VICILIN.

	36	38	39
Carbon	52.43	52.20	52.45
Hydrogen	7.04	7.01	7.04
Nitrogen	17.45	17.53	17.22
Sulphur	0.23	0.15	0.16
Oxygen	22.85	23.11	23.13
	100.00	100.00	100.00

The reactions of legumin and vicilin will be given fully in a following paper after describing the preparation of these proteids from other legumes.

On page 349 we described how, after dialyzing for four days, the solution of the precipitate obtained by saturating the seed extract with ammonium sulphate, the greater part of the glob-

ulin was precipitated, and stated that the solution filtered from this globulin, there marked A, was reserved for further notice. This solution, which by dialysis had become bulky, was saturated with ammonium sulphate and the precipitate produced, filtered out, suspended in a little water and dialyzed over night. In this way the proteids were concentrated in a small volume of liquid. This solution was then filtered clear and dialyzed. After five days the precipitate which had separated was filtered out and extracted with ten per cent. salt solution, but as only very little dissolved, it was washed free from chlorides with water, then with alcohol and dried at 110°. Analysis showed it to have the following composition:

LEGUMELIN, 40.

Carbon	52.93
Hydrogen	7.10
Nitrogen	16.18
Sulphur	0.85
Oxygen	22.94
	100.00
Ash	0.22

The filtrate from 40 was then saturated with ammonium sulphate and the precipitate produced, dissolved in as small a volume of water as possible, filtered clear and dialyzed seven days. A very slight precipitate separated which was filtered out, washed thoroughly with water and found to dissolve in ten per cent. brine, giving a solution which yielded a flocculent coagulum at 53°; the heat coagulation point of the body we designate *legumelin*. The solution from which this small precipitate had separated, after filtering, was heated in a water-bath to 67° and a large coagulum produced which was washed thoroughly with hot water and then with alcohol and dried over sulphuric acid, giving eighteen grams of 41.

The filtrate from 41 was heated to 95° and the resulting coagulum, washed and dried, formed preparation 42, weighing 4.10 grams. Dried at 110° these gave the following results when analyzed:

LEGUMELIN.

	41	42
Carbon	53.24	53.36
Hydrogen	6.99	6.98
Nitrogen	16.15	16.24
Sulphur	1.09	1.01
Oxygen	22.53	22.41
	100.00	100.00
Ash	0.21	0.21

Another extract, obtained in substantially the same manner as that just described, after removing most of the globulin by dialysis, was saturated with ammonium sulphate and the precipitate produced was dissolved in a little water and its solution dialyzed for seven days, giving a precipitate which was filtered out and found to consist almost wholly of proteid matter insoluble in salt solution. After extracting with brine, this substance was thoroughly washed with water and dried, giving 4.24 grams of preparation 43. The filtrate from 43 was dialyzed in pipe water for five days longer, but as no more precipitate resulted, it was dialyzed for five days in a large volume of distilled water, which was frequently changed and kept cool by adding ice containing only an extremely small quantity of mineral matter. No precipitate was thus separated, and to the solution was then added ten per cent. of sodium chloride and acetic acid as long as a precipitate formed. The resulting precipitate was filtered out, dissolved in water and sodium carbonate added to very slight alkaline reaction. This caused a large precipitate which when prepared for analysis weighed 5.73 grams, preparation 44. The solution filtered from this neutralization precipitate, contained only a very little proteid, as shown by saturating the filtrate with ammonium sulphate.

The filtrate from the precipitate produced by acetic acid in the ten per cent. salt solution was unchanged on further addition of acetic acid and was therefore saturated with sodium chloride which gave a second precipitate. This was filtered out, dissolved in water, the solution filtered clear and dialyzed. After chlorides had diffused away the solution was perfectly neutral to litmus and quite clear. It was accordingly concentrated by dialysis in alcohol and the precipitated proteid, 45, dehydrated

by absolute alcohol, and dried, weighed 5.87 grams. These preparations were analyzed with the following results :

LEGUMELIN.

	43	44	45
Carbon	53.03	53.43	53.23
Hydrogen	7.10	7.01	6.91
Nitrogen	16.30	16.50	16.08
Sulphur	1.01	1.16	1.11
Oxygen	22.56	21.90	22.67
	100.00	100.00	100.00
Ash	0.35	0.80	0.56

It will soon be shown that the proteose of the pea is precipitated by acetic acid from a solution saturated with sodium chloride, and it might be expected that 45 would therefore contain a large proportion of proteose; but as it was found that this preparation through washing with alcohol and drying at 110° had become insoluble in water, it is probable that the proteose had mostly diffused away during the long dialysis to which the solutions had been subjected.

If the last six analyses are compared, it will be seen that they are in close agreement except 40, in which carbon and sulphur are somewhat lower, due we think to the presence of a little vicilin which might be expected to be present, owing to the method of preparation. To facilitate comparison the other five analyses are arranged in the following table together with those of 5 and 8 described in our former paper.

LEGUMELIN.

	5	8	41	42	43	44	45	Aver.
Carbon	53.33	53.54	53.24	53.36	53.03	53.43	53.23	53.31
Hydrogen	6.98	6.99	6.99	6.98	7.10	7.01	6.91	6.99
Nitrogen	16.14	16.69	16.15	16.24	16.30	16.50	16.08	16.30
Sulphur	1.00	1.01	1.09	1.01	1.01	1.16	1.11	1.06
Oxygen	22.55	21.77	22.53	22.41	22.56	21.90	22.75	22.34
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

5 and 8, coagulated by alcohol.
41, coagulated by heat at 67°.
42, coagulated by heat at 95°.
43, coagulated by dialysis in water.

44, precipitated by acetic acid from ten per cent. salt solution.

45, precipitated by acetic acid from saturated salt solution.

The properties and reactions of legumelin will be discussed later after describing its occurrence in other seeds.

Returning to the first extract, the filtrate from 42 contained nothing coagulable on boiling. It was therefore dialyzed in alcohol and so concentrated to small volume. A quantity of proteid was thus precipitated which was filtered out and washed with absolute alcohol. The substance thus obtained, weighing 10.5 grams after drying over sulphuric acid, was dissolved in 100 cc. of water, with which it gave a clear solution, and sodium chloride was added to saturation, which caused a slight precipitate. This was filtered out, but owing to its small amount was not further examined. The filtered solution was then treated with salt-saturated acetic acid as long as a precipitate was produced, which required a relatively large amount of acid. The resulting gummy precipitate was washed with saturated salt solution, dissolved in water, the solution neutralized with a little sodium carbonate and dialyzed till free from chlorides, when the dialyzer was transferred to alcohol and the solution concentrated to small volume. The substance thus precipitated was filtered out, extracted thoroughly with absolute alcohol and dried over sulphuric acid giving 4.06 grams of preparation 46, having, when dried at 110°, the composition here given.

PROTEOSE, 46.

Carbon	50.24
Hydrogen	6.96
Nitrogen	17.35
Sulphur	1.25
Oxygen	24.40
	100.00
Ash	0.92

The solution, filtered from 46, which had been thrown down by the addition of acetic acid to the solution saturated with salt, was neutralized with sodium carbonate, of which a large quantity was required, showing that only a small proportion of the acid had been precipitated with the proteose. This neutralized solution was dialyzed in water until free from chlorides and then con-

centrated by dialysis in alcohol. The substance thus precipitated was filtered out, washed with absolute alcohol, dried and found to weigh 1.76 grams. This, dried at 110°, gave the following results when analyzed :

PROTEOSE, 47.

Carbon	49.66
Hydrogen	6.78
Nitrogen	16.57
Sulphur	1.40
Oxygen	25.59
	100.00
Ash	3.20

Preparations 46 and 47 give precipitates with copper sulphate which yield the usual rose-red biuret reaction on adding potash. With nitric acid they give no precipitates but yield yellow solutions on warming. If the solution is first saturated with salt, 46 gives a heavy precipitate with nitric acid which largely dissolves on heating and reprecipitates on cooling, while 47 under like conditions gives only a turbidity diminished by adding an excess of acid.

We have then in the pea the following proteids :

Legumin, a globulin not coagulated by heating its solutions.

LEGUMIN.

Carbon	51.74[1]
Hydrogen	6.90
Nitrogen	18.04
Sulphur	0.42
Oxygen	22.90
	100.00

Vicilin, a globulin soluble in a more dilute brine than legumin, coagulated on heating its solutions to 95°–100° and having the following composition :

VICILIN.

Carbon	52.36
Hydrogen	7.03
Nitrogen	17.40
Sulphur	0.18
Oxygen	23 03
	100.00

[1] This figure for carbon is about four-tenths per cent. lower than that given in our former paper, a difference which we attribute to the fact that this preparation was made from a neutralized solution and that vicilin had been separated from it completely.

Legumelin, a proteid partially precipitated by dialysis, generally in a coagulated state, the greater part however remaining in solution even after prolonged dialysis. Whether it should be called a globulin or an albumin is perhaps questionable, but its relations seem to be closer to the albumins than to the globulins. Its composition as shown by the average of the analyses of five preparations obtained by three different methods, is:

LEGUMELIN.

Carbon	53.31
Hydrogen	6.99
Nitrogen	16.29
Sulphur	1.06
Oxygen	22.35
	100.00

A *Protoproteose* precipitated by acetic acid from its solution saturated with salt:

PROTOPROTEOSE.

Carbon	50.24
Hydrogen	6.76
Nitrogen	17.35
Sulphur	1.25
Oxygen	24.40
	100.00

A *deuteroproteose* not precipitated by acetic acid from the salt saturated solution:

DEUTEROPROTEOSE.

Carbon	49.66
Hydrogen	6.78
Nitrogen	16.57
Sulphur	1.40
Oxygen	25.59
	100.00

The combined amount of legumin and vicilin which we have obtained by dialyzing extracts of the pea was about ten per cent., as the following experiments show.

Of the finely ground pea meal, 200 grams were treated with one liter of water, the mixture poured on a coarse sieve and the

lumps broken up and washed through with another liter of water. After standing over night, in a cool place, protected with thymol, the suspended matters settled leaving a somewhat turbid solution, of which 1500 cc. were siphoned off and filtered on a pulp filter. The first 300 cc. which passed through the filter were rejected, as they were mixed with the water contained in the pulp. The next liter of clear solution was dialyzed until all that could be thus precipitated had separated in the form of minute spheroids. In this way there was obtained a quantity of proteid which weighed 4.35 grams when washed with alcohol and dried over sulphuric acid. The extract from which this was separated was one-half the total and therefore corresponded quite nearly to that yielded by 100 grams of meal, thus showing that 4.35 per cent. thereof was extracted by distilled water and precipitated by dialysis.

The meal residue (from which, as described, three-fourths of the extract had been siphoned), together with the still adhering one-fourth of the extract, was treated with ten per cent. salt solution until the volume was 2000 cc. After settling, the solution was siphoned off, filtered perfectly clear, and dialyzed until all the globulin was precipitated. In this way 9.83 grams of globulin were obtained. As the meal residue before this extraction contained one-fourth of the water extract there should have been present 2.18 grams of proteid soluble in water and precipitable by dialysis. As three-fourths of the total salt extract yielded the above 9.83 grams there should be deducted therefrom three-fourths of 2.18 grams or 1.64 grams, making 8.19 grams of globulin obtained from three-fourths of 200 grams of meal or 5.46 per cent. which added to 4.35 per cent. makes 9.81 per cent. total globulin.

To another lot of 100 grams of meal 500 cc. of water were added, containing just enough baryta to produce an extract reacting neutral to litmus and to this 500 cc. of ten per cent. salt solution were added. From 750 cc. of this extract filtered clear, 7.33 grams of globulin separated on dialysis, equal to 9.77 per cent. of the meal. In another experiment, carried out in essentially the same manner, 10.0 per cent. of globulin was obtained.

By treating the residual meal with alkali but very little more proteid was dissolved. On digesting pea meal with ten times its

weight of one-tenth per cent. soda solution, a gelatinous mass resulted from which no clear extract could be obtained. If however a baryta solution of equal molecular strength was used the extract was readily filtered. From such an extract, filtered perfectly clear, there was obtained by adding acetic acid in slight excess 10.56 per cent. of proteid and by dialyzing the filtrate therefrom 3.16 per cent. more. Whether this 13.72 per cent. of proteid was substantially all legumin and vicilin we have no means of knowing. In the first of these experiments it will be noticed that 4.35 per cent. of globulin was obtained by dialyzing the aqueous extract. As the water used in this extraction weighed ten times as much as the meal the saline solution resulting from the mineral constituents of the seed would be so exceedingly dilute as to make it seem doubtful that so much globulin could be thereby dissolved. The reactions of this extract were therefore studied with a view to determine if possible the cause of the solution of the proteid.

When the extract was cautiously poured into distilled water a faint cloud formed at the point of contact of the two liquids which wholly disappeared on shaking. Under similar conditions a globulin solution commonly gives a permanent turbidity. Sodium chloride carefully and very gradually added, beginning with a minute quantity, gave no trace of a precipitate until the solution was saturated with the salt, when a very little proteid separated. A little acetic acid gave a precipitate completely dissolving on adding sodium chloride. If however a somewhat greater quantity of acid was added the precipitate did not wholly dissolve. By cautiously adding very dilute sodium carbonate solution even up to strong alkaline reaction no trace of a precipitate was observed.

Baryta solution when added in considerable quantity gave a little precipitate, probably due to phosphates. Calcium chloride gave a slight precipitate soluble in an excess of calcium or sodium chlorides. Calcium sulphate gave no precipitate.

From this it will be seen that solution of the globulin is apparently not due to the presence of acids, for neutralization gives not even a turbidity, nor to the presence of neutral salts since dilution does not give a permanent precipitate.

An extraction, with water containing just enough baryta to

leave the solution neutral to litmus, was made exactly like that described. This gave 3.75 per cent. of globulin on dialysis as against 4.35 per cent. extracted with water alone. By heating the filtrate from the above-mentioned preparation to 85° and washing and drying the coagulum, the amount of legumelin was found to be 2.03 per cent. of the meal.

PROTEIDS OF THE LENTIL.[1]

BY THOMAS B. OSBORNE AND GEORGE F. CAMPBELL.

Received March 29, 1898.

THE proteid substance of the lentil was first observed by Einhof in 1806[2]. Liebig[3] stated that plant-casein is obtained from beans, lentils, and peas. Dumas and Cahours[4] extracted lentils with warm water, allowed the extract to deposit suspended impurities and precipitated the proteid from the decanted solution by adding acetic acid. After washing the substance thus separated with water and alcohol and drying it, they obtained the following figures by analysis:

Carbon	50.46
Hydrogen	6.65
Nitrogen	18.19
Oxygen, etc.	24.70
	100.00

Ritthausen[5] described a single preparation of proteid from this seed, obtained in nearly the same way as the preceding, for which he gave the following composition:

Carbon	52.53
Hydrogen	6.84
Nitrogen	16.49
Sulphur	0.40
Oxygen	23.74
	100.00

For our work, coarsely ground lentils were freed almost completely from the outer seed coats by a current of air and were then

[1] Reprinted from advance sheets of the Report of the Connecticut Agricultural Experiment Station for 1897. Communicated by the authors.

[2] Gehlen's *J. der Chem.*, 6, 543.

[3] *Ann. Chem. Pharm.*, 39, 138.

[4] *J. prakt. Chem.*, 28, 398.

[5] Die Eiweisskörper, etc., Bonn, 1872.

ground to a fine flour. Two kilograms of this flour were treated with ten liters of ten per cent. sodium chloride solution and after a short time the extract was strained out on fine bolting-cloth and allowed to stand over night in a cold place to deposit the suspended starch. The partly clarified extract was then passed through a centrifugal separator and finally filtered perfectly clear through a thick bed of filter-paper pulp. The extract was saturated with ammonium sulphate, the precipitate produced dissolved in dilute brine, the solution filtered perfectly clear and dialyzed for three days.

The globulin that had separated on dialysis was filtered out and, after washing with water and alcohol, dried over sulphuric acid. Preparation[1] 48 was thus obtained, which weighed 170 grams.

The solution from which 48 had separated was dialyzed for six days longer when it was filtered from a very small precipitate which, when washed and dried, formed preparation 49 that weighed 2.12 grams. The filtrate from 49 was saturated with ammonium sulphate, the separated proteid filtered out, dissolved in water, the solution filtered clear, and dialyzed. After prolonged dialysis but a trace of substance separated, which was filtered out, and the clear solution dialyzed in alcohol until all the proteid was precipitated. The substance thus obtained after drying weighed 6.78 grams. It was ground fine, exhausted with water and washed with alcohol, forming preparation 50.

These preparations were dried at 110° to constant weight and analyzed with the following results:

	48[1]	49	50
Carbon	51.59	52.12	53.31
Hydrogen	6.99	6.88	6.71
Nitrogen	17.63	16.21	16.08
Sulphur	0.56	0.79	0.97
Oxygen	23.23	24.00	22.93
	100.00	100.00	100.00
Ash	0.49	0.79	0.74
Amount	170.0 grams	2.12 grams	6.78 grams.

[1] Numbered consecutively with the preparations of the proteids of the pea. This Journal, 19, 494.

In order to subject 48 to fractional precipitation one hundred grams were treated with 250 cc. of water and 250 cc. of ten per cent. brine added. A large part failed to dissolve, having been converted into an insoluble form by the process of separation. This part was collected on filters, washed with cold five per cent. brine, and then with hot brine of the same strength, the cold and hot washings being kept separate. The residue was next washed with water and with alcohol and dried, giving 62.23 grams of preparation 51. The washings made with hot brine were diluted with four volumes of water so as to form a one per cent. salt solution and the precipitate produced allowed to settle, when the solution was decanted and the deposit washed with water and alcohol and dried, yielding preparation 52, weighing 3.28 grams.

The solution filtered from 51, which measured 300 cc., was mixed with the cold washings, and diluted until the solution contained two per cent. of salt. The rapidly settling precipitate which separated was washed with water and with alcohol, and when dried weighed 4.75 grams, preparation 53.

The solution decanted from 53 was treated with an equal volume of water making a one per cent. brine, whereby substance was separated which, when washed and dried in the usual way, gave 9.5 grams of preparation 54.

The filtrate from 54 was cooled during the night to about 5° which caused a further deposit, that by the usual treatment gave 7.69 grams of preparation 55.

So large a proportion of 48 had become insoluble in salt solution, that it was thought best to make another lot of the globulin, which if possible should be more soluble. Accordingly 1000 grams of lentil flour were extracted with ten per cent. brine and the globulin separated by dialysis in exactly the same way as employed in making 48. Instead, however, of washing the substance on the filter with alcohol it was removed from the paper, redissolved in five per cent. brine, and the filters washed with the same solution. The filtrate and washings measured 800 cc. As 600 cc. of five per cent. brine had been used this solution contained thirty grams of salt. To this was added one liter of water, so that the resulting mixture contained 1.66 per cent. of sodium chloride and had a temperature of 25°. The large pre-

cipitate that appeared, soon settled to a coherent layer on the bottom of the jar, so that the solution, very nearly clear, could be decanted almost completely. The deposit was thoroughly washed with water and with alcohol, and after drying weighed 21.43 grams, preparation 56.

The solution decanted from 56 was cooled over night to 5°. The proteid separated as a dense semitransparent deposit which on washing with water became opaque and white. It was then dehydrated with absolute alcohol and dried, giving 16.10 grams of preparation 57.

The filtrate from 57 was dialyzed for four days whereby chlorides were completely separated. A coherent layer of globulin, which was deposited on the bottom of the parchment bag, when washed and dried weighed 32.8 grams and formed preparation 58.

These preparations were dried to constant weight and analyzed with the following results :

GLOBULIN.

	51	52	53	54	55	56	57	58
Carbon	51.52	51.43	51.44	51.62	52.13	51.53	51.39	52.05
Hydrogen	6.96	6.91	6.96	7.01	7.19	6.86	6.98	7.02
Nitrogen	17.69	18.02	17.99	17.87	17.47	18.06	18.03	17.29
Sulphur	0.50 }	23.64	0.44	0.46	0.23	0.49	0.44	0.21
Oxygen.....	23.33 }		23.17	23.04	22.98	23.06	23.16	23.43
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Ash.....	0.94	0.61	1.43	0.33	0.29	0.61	0.14	0.08

In this seed, as in the pea, we thus found that by fractional precipitation, the globulin is separated into two parts which differ in composition and solubility. As however none of the less soluble fractions was wholly free from coagulable matter, another extraction was made in which the acid of the seed was neutralized and the fractional precipitations were repeated until products wholly free from coagulable proteid were obtained.

Accordingly 2000 grams of meal were treated with ten liters of ten per cent. salt solution in which had been dissolved sufficient potash to yield an extract neutral to litmus, as determined by a preliminary trial. After thoroughly mixing, the whole was allowed to stand over night, with thymol, in a cool place, when the partly cleared extract was siphoned off and filtered. The solution was then saturated with ammonium sulphate, the pre-

cipitate filtered out, suspended in water and dialyzed over night. The proteid was thus dissolved, the solution filtered perfectly clear and dialyzed in two parts. Part I, which was obtained first, was treated as follows:

After dialyzing four days the precipitated globulin was filtered out and the filtrate A treated as subsequently described. The precipitate was dissolved in 500 cc. of two per cent. salt solution and 500 cc. of water added. A large precipitate formed, from which, after settling, the solution B was decanted.

The precipitate was then dissolved in 400 cc. of two per cent. salt solution and precipitated again by adding 400 cc. of water. The solution C was decanted from the precipitate thus thrown down, and the latter dissolved in five per cent. salt solution, and found to yield a considerable coagulum on heating in a boiling water-bath, showing it to still contain some vicilin. This latter solution was filtered clear and dialyzed for three days, when the precipitate which had formed was dissolved in 300 cc. of two per cent. salt solution, and 100 cc. of water added, causing a large precipitate which was found to be entirely free from coagulable matter. After washing this with water and alcohol, and drying over sulphuric acid, 23.67 grams of preparation 59 were obtained having the following composition when dried at 110°:

LEGUMIN 59.

Carbon	51.80
Hydrogen	6.86
Nitrogen	18.09
Sulphur	0.42
Oxygen	22.83
	100.00
Ash	0.29

The solution decanted from 59 was treated with 200 cc. of water and the precipitate produced allowed to settle. The solution was then decanted and the precipitate washed with water and alcohol giving 5.36 grams of preparation 60, which, when dried at 110° and analyzed, gave the following results:

GLOBULIN, 60.

Carbon	51.83
Hydrogen	7.01
Nitrogen	17.75
Sulphur	0.29
Oxygen	23.12
	100.00
Ash	0.46

The solution decanted from 60 was dialyzed free from chlorides and the precipitate thereby separated, after washing and drying as usual, gave preparation 61, which analysis showed to contain:

VICILIN, 61.

Carbon	52.13
Hydrogen	6.95
Nitrogen	17.40
Sulphur	0.22
Oxygen	23.30
	100.00
Ash	0.21

Solution B, page 366, was diluted with an equal volume of water which caused a precipitate, from which, after settling, the solution was decanted. This was washed, dried, and analyzed with the following results:

VICILIN, 62.

Carbon	52.28
Hydrogen	7.02
Nitrogen	17.41
Sulphur	0.08
Oxygen	23.21
	100.00
Ash	0.21

The filtrate from this preparation was saturated with ammonium sulphate, but very little proteid was found in it.

Solution C, page 366, was also treated with an equal volume of water which precipitated a further quantity of globulin, that, when dried, weighed 5.55 grams, and had the following composition:

VICILIN, 63.

Carbon	52.14
Hydrogen	7.02
Nitrogen	17.27
Sulphur	0.18
Oxygen	23.39
	100.00
Ash	0.21

Solution A, described on page 366, from which the greater part of the globulin extracted from the meal, had been removed by dialysis, was saturated with ammonium sulphate. The precipitate produced was suspended in water and dialyzed over night, thereby bringing the proteid into solution in a comparatively small volume of water. This solution was then filtered perfectly clear, and dialyzed forty hours, when a considerable precipitate separated which was filtered out, washed, dried, and analyzed with results as follows:

VICILIN, 64.

Carbon	52.03
Hydrogen	6.91
Nitrogen	17.60
Sulphur	0.13
Oxygen	23.33
	100.00
Ash	0.26

The filtrate from 64, after uniting with the similar solution from part II of this extract, was further dialyzed for nine days, until free from sulphates, when the precipitate which had formed was filtered out, washed, dried, and analyzed; It weighed only 1.13 grams and had the following composition:

LEGUMELIN, 65.

Carbon	53.02
Hydrogen	——
Nitrogen	16.36
Sulphur } Oxygen }	——
Ash	0.47

The clear solution filtered from 65 was then heated in a water-bath for three hours at 65° and the resulting coagulum filtered

out and the filtrate further heated to 82°, whereby a second coagulum was produced. These two preparations, 66 and 67 respectively, were washed with hot water and with absolute alcohol and gave on analysis, when dried at 110°, the following results :

LEGUMELIN.

	66	67
Carbon	53.33	53.23
Hydrogen	6.87	6.88
Nitrogen	16.28	16.35
Sulphur	0.85	1.00
Oxygen	22.67	22.54
	100.00	100.00
Ash	0.20	0.41

The filtrate from 67 was concentrated by dialysis in alcohol and the proteid so precipitated filtered out, washed with absolute alcohol, and redissolved in a little water. This solution was dialyzed and found wholly free from globulin, and also from coagulable proteid. The solution was then precipitated by pouring into much alcohol and the substance so separated dried and analyzed.

PROTEOSE, 68.

Carbon	50.17
Hydrogen	6.77
Nitrogen	16.81
Sulphur	1.27
Oxygen	24.98
	100.00
Ash	1.03

As already stated, the solution of the first ammonium sulphate precipitate of the proteids contained in the original extract was divided into two parts, which were dialyzed separately. The precipitate so produced in part II was dissolved in 500 cc. of two per cent. brine and 750 cc. of water added, giving an abundant precipitate, which was washed with water and alcohol and dried over sulphuric acid. This preparation, 69, wholly free from coagulable proteid, weighed nineteen grams and had, when dried at 110°, the following composition :

LEGUMIN, 69.

Carbon	51.91
Hydrogen	7.11
Nitrogen	17.91
Sulphur	0.38
Oxygen	22.69
	100.00
Ash	0.62

In order to further fractionate preparations 59 and 69, quantities of each were mixed together, dissolved in five per cent. salt solution and filtered from a very small amount of insoluble matter. That any acid possibly present in combination with this globulin might be neutralized, three-tenths per cent. potash solution was cautiously added until the solution reacted just perceptibly alkaline with litmus paper. This solution was then dialyzed over night and the precipitate which separated was filtered out and the filtrate dialyzed twenty-four hours longer, giving a second precipitate, which was washed and dried as usual, forming preparation 70, while the first dialytic precipitate was redissolved in ten per cent. brine, filtered perfectly clear and again dialyzed over night. The precipitate which separated was prepared for analysis in the usual manner and formed preparation 71. These two products were found to be free from coagulable matter and to have the following composition, which is essentially the same as that of the preparations from which they originated:

LEGUMIN.

	70	71
Carbon	51.85	51.74
Hydrogen	6.88	6.87
Nitrogen	18.07	18.09
Sulphur	0.37	0.39
Oxygen	22.83	22.91
	100.00	100.00
Ash	0.56	0.44

Since legumin has been described as soluble in water, 400 grams of lentil meal were twice treated with two liters of water, and strained on bolting-cloth. The extract was allowed to settle over night, and the somewhat turbid liquid (four liters) was siphoned off and saturated with ammonium sulphate. The precipitated proteids were treated with dilute brine, in which nearly

all dissolved. The solution was filtered clear and dialyzed for forty hours; the resulting precipitate, weighing, when dried, seven grams, was analyzed with the following results:

LEGUMIN, 72.

Carbon	51.65
Hydrogen	6.90
Nitrogen	18.05
Sulphur	0.38
Oxygen	23.02
	100.00
Ash	0.64

One more extraction was made in the following manner: To 1200 grams of lentil meal, six liters of water were added which held in solution, 6.21 grams of baryta, the amount which had previously been determined to yield an extract neutral to litmus. After thoroughly mixing with the meal and breaking up all the lumps, six liters of ten per cent. salt solution were added. Unlike extracts not neutralized or neutralized with soda or potash, the insoluble matter in this case formed large flocculent masses which rapidly settled. The insoluble matter was strained out on bolting-cloth and the nearly clear extract was saturated with ammonium sulphate. The proteid thus separated was filtered out, dissolved in water, and dialyzed for three days. The greater part of the globulin was thus separated. It was filtered out and the filtrate was treated as described on page 372. The precipitate was dissolved in two per cent. brine and diluted until the solution contained 1.25 per cent. of salt. After depositing the resulting precipitate the solution was decanted and the precipitate was five successive times redissolved in fifty cc. of ten per cent. brine and thrown down by diluting to 400 cc. with water. The final precipitate, which was free from coagulable globulin, was washed with water and alcohol and dried. It weighed 15.85 grams and had the following composition:

LEGUMIN, 73.

Carbon	51.63
Hydrogen	6.95
Nitrogen	18.00
Sulphur	0.43
Oxygen	22.99
	100.00
Ash	0.33

The solutions, resulting from the five just mentioned precipitations, and containing about one per cent. of salt, were diluted with an equal volume of water, forming a one-half per cent. salt solution. Proteid was thus precipitated which when dry weighed 20.25 grams, but was not further examined as it was doubtless a mixture of legumin and vicilin. The solution decanted from the foregoing precipitate was dialyzed for four days whereby 9.35 grams of preparation 74 were obtained having the following composition:

VICILIN, 74.

Carbon	52.15
Hydrogen	6.81
Nitrogen	17.21
Sulphur	0.14
Oxygen	23.69
	100.00
Ash	0.26

The filtrate described on page 371 from which the greater part of the globulin present in the extract had been separated by dialysis, was saturated with ammonium sulphate, the precipitate produced dissolved in a little water, and the solution filtered clear and dialyzed for seven days, when it was filtered from a small precipitate which analysis showed to be probably a mixture of vicilin and legumelin. The solution was returned to the dialyzer and the dialysis continued several days but nothing more separated. The solution was then concentrated by dialysis in alcohol and the precipitated proteid was dehydrated with absolute alcohol and dried. This preparation was then extracted with water, the residue remaining washed with alcohol, dried, and analyzed:

LEGUMELIN, 75.

Carbon	53.10
Hydrogen	6.91
Nitrogen	16.16
Sulphur	1.09
Oxygen	22.74
	100.00
Ash	0.56

It is thus evident that the lentil contains the same proteids as the pea; *viz.*, egumin, vicilin, legumelin, and proteose.

In the following tables are brought together the analyses of the numerous preparations of these proteids, so that they may be easily compared.

LEGUMIN.

	52	53	54	55	56
Carbon	51.43	51.44	51.62	51.53	51.39
Hydrogen	6.91	6.96	7.01	6.86	6.98
Nitrogen	18.02	17.99	17.87	18.06	18.03
Sulphur }	23.64	0.44	0.46	0.49	0.44
Oxygen }		23.17	23.04	23.06	23.16
	100.00	100.00	100.00	100.00	100.00
	59	70	71	72	73
Carbon	51.80	51.85	51.74	51.65	51.63
Hydrogen	6.86	6.88	6.87	6.90	6.95
Nitrogen	18.09	18.07	18.09	18.05	18.00
Sulphur	0.42	0.37	0.39	0.38	0.43
Oxygen	22.83	22.83	22.91	23.02	22.99
	100.00	100.00	100.00	100.00	100.00

As the five analyses standing last in the above table were made on preparations obtained from neutralized solutions and free from coagulable proteids, we consider them to represent the composition of lentil legumin most accurately, and accordingly we give the following average of these analyses for the composition of this substance.

LENTIL LEGUMIN.

Carbon	51.73
Hydrogen	6.89
Nitrogen	18.06
Sulphur	0.40
Oxygen	22.92
	100.00

VICILIN.

	55	58	61	62	63	64	74	Aver.
Carbon	52.13	52.05	52.13	52.28	52.14	52.03	52.15	52.13
Hydrogen	7.19	7.02	6.95	7.02	7.02	6.91	6.81	6.99
Nitrogen	17.47	17.29	17.40	17.41	17.27	17.60	17.21	17.38
Sulphur	0.23	0.21	0.22	0.08	0.18	0.13	0.14	0.17
Oxygen	22.98	23.43	23.30	23.21	23.39	23.33	23.69	23.33
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

LEGUMELIN.

	50	65	66	67	75	Average.
Carbon	53.31	53.02	53.33	53.23	53.10	53.20
Hydrogen .	6.71	....	6.87	6.88	6.91	6.82
Nitrogen...	16.08	16.36	16.28	16.35	16.16	16.25
Sulphur ...	0.97	...	0.85	1.00	1.09	0.98
Oxygen....	22.93	....	22.67	22.54	22.74	22.75
	100.00	.....	100.00	100.00	100.00	100.00

PROTEOSE, 68.

Carbon	50.17
Hydrogen	6.77
Nitrogen	16.81
Sulphur	1.27
Oxygen	24.98
	100.00

The quantity of proteid extracted by water and precipitated by dialysis was determined for the lentil, as follows :

To 200 grams of fine ground meal one liter of water was added; the mixture was poured upon a sieve and the lumps broken up by washing them through with another liter of water. After mixing and standing a short time, the coarse residue was strained out on bolting-cloth, and the fine suspended matter allowed to settle over night at a low temperature. The solution was then siphoned off, filtered perfectly clear on a pulp filter, the first 300 cc. containing the water retained in the pulp being rejected, and one liter of the clear undiluted extract next passing the filter dialyzed as long as anything precipitated. In this way 9.76 per cent. of proteid was recovered, which contained 17.32 per cent. of nitrogen, showing the substance to be nearly pure globulin.

This operation was repeated with the same quantities and proportions of materials, but with the addition of just enough baryta to the water to give an extract perfectly neutral to litmus. On dialysis 13.72 per cent. of globulin was obtained, a considerably larger quantity than that yielded by the unneutralized extract. Although the globulins extracted from the lentil by brine are legumin and vicilin, identical in composition and properties with those from the pea, yet the proportion extracted by water from

the lentil is much greater, especially when the acid of the seed is neutralized to litmus.

A rigid comparison of the reactions given by the aqueous extracts of the lentil, both acid and neutral, showed no difference whatever, and in these reactions the extracts agreed strictly with those similarly obtained from the pea, except that with calcium chloride and sulphate heavy precipitates were obtained, readily soluble in a slight excess of calcium or sodium chloride. Extracts of the pea gave only slight precipitates with calcium chloride and none with calcium sulphate.

ON THE SPEED OF COAGULATION OF COLLOID SOLUTIONS.

By C. E. Linebarger.

Received April 2, 1898.

ONE of the prettiest of projection experiments is the exhibition of the formation of crystals of salts, as ammonium chloride and oxalate, etc. The crystals seem fairly to shoot out over the screen. This speed of crystallization, so strikingly shown by the lantern, appears to be a characteristic property of solutions varying with the nature of the salt and solvent, the temperature, the degree of supersaturation, etc. So far as I know, no careful quantitative work has ever been done on the subject; some rough determinations that I have made with solutions of potassium nitrate indicate that the speed of crystallization is one or two millimeters per second.

Although there is a dearth of data on the subject, it will probably be conceded that the speed with which crystalloidal substances separate out of solution, is comparatively rapid; that is to say, the crystallizing solid traverses appreciable distances in a second or so.

Crystallization does not supervene unless the solution be supersaturated with respect to the solid, and there be at least a trace of a crystal already present to induce the crystallization; a supersaturated solution is then in an unstable condition.

Solutions of many colloids can be made to coagulate or gelatinize by the addition of a mere trace of certain substances. The striking analogy between this phenomenon and that of crystallization has often been mentioned and insisted

upon. Solutions of colloids behave as if they were supersaturated and required but a chance to pass over into the solid condition. We cannot expect the speed of coagulation to be very great, for we know how slow is the diffusion of colloids in solution. Still, if there is a true analogy between the processes of crystallization and coagulation, the addition of a small amount of a substance having the power to start coagulation in one part of a colloid solution should result in the spread of the coagulation at a certain rate throughout the whole solution, just as happens in the case of crystalloids in supersaturated solution.

The following experiments have been performed with the object in view of ascertaining whether the analogy presumed to exist in the behavior of solutions of colloids and of supersaturated solutions of crystalloids can stand the test of a severer scrutiny than has yet been accorded it.

PRELIMINARY EXPERIMENTS.

Two glass tubes of about five mm. bore were bent twice at right angles so as to form wide ∐-tubes; they had almost identical shapes. These tubes were held in a support side by side, and filled with a solution of colloidal iron prepared as follows:

To a very strong solution of pure ferric chloride in water, an almost saturated solution of ammonium carbonate was added in small portions with thorough agitation until the point of permanent precipitation was nearly reached. The resulting dark red solution was subjected to dialysis in parchment paper tubes until the outside water after twenty-four hours' contact with the tubes showed but faint traces of chlorine.

An analysis of the solution showed that it contained 20.563 grams iron and 7.128 grams chlorine to the liter; as is seen, a not inconsiderable amount of chlorine had refused to pass through the parchment paper.

A thin glass rod was dipped into dilute sulphuric acid, the drop clinging to it when removed was shaken off, and then the end on which but a faint trace of the acid remained was touched to the surface of the solution of iron; coagulation at once supervened at the surface. The tubes were then carefully stopped up with plugs of wax.

The accompanying table summarizes the observations of the

position of the coagulum after certain time-intervals and the speed of propagation of the coagulation; this speed is the ratio of the distance in centimeters passed over by the coagulum to the time in seconds between two observations. No provision was made for keeping the temperature constant, which may have varied by as much as 15°–20°. The behavior of the solution in both tubes was very nearly the same, so that their mean is given.

SPEED OF PROPAGATION OF COAGULATION OF COLLOID IRON SOLUTIONS.

Time in seconds.	Distance in centimeters.	Speed.
36×10^2	0.30	833×10^{-7}
210	0.70	402
470	0.55	212
734	0.25	94
877	0.10	71
1308	0.35	80
*2641	*0.55	41
3505	0.15	17
4368	0.10	2
6096	0.11	5
14736	0.12	1
43656	0.20	0.8

The table shows that the speeds decrease continually until they practically vanish. The greater speeds at the beginning of the experiment are probably due to the diffusion of the sulphuric acid. It seems not at all unlikely that sulphuric acid enters into chemical combination with dissolved colloidal iron, forming an insoluble compound; a comparatively small amount of the acid suffices to neutralize and precipitate a large quantity of iron oxide in the colloid state. Whitney's[1] experiments on certain compounds of chromium sulphate seem to be in accord with this view. If it be true, the precipitation of colloids from solution is not a physical phenomenon of supersaturation, but rather one of chemical combination.

It was thought that possibly the exceedingly small speed observed after the lapse of several days (marked with stars in the table) was not due to the spread of the coagulation but to mechanical jarring and gravity, for the coagulum was in the vertical portion of the tubes and the laboratory was subject to considerable jarring from the busy traffic of the street. The

[1] *Ztschr. phys. Chem.*, 20, 40, *1896*.

appearance of the coagulum seemed to confirm this, for at the end of the time marked with a star in the table, it had lost the resemblance it at first had to a stack of inverted hollow cones fitting loosely into one another and had assumed the form of piles of disks like rouleaux of coins. In subsequent experiments only horizontally placed tubes were employed in a room quite free from mechanical vibrations.

DESCRIPTION OF APPARATUS.

A glass tube of about a millimeter bore and twenty cm. in length was fused in the side of a six-inch test-tube so as to be perpendicular to its axis; its extremity was drawn out in a long capillary and turned up through a right angle. A millimeter scale was attached to the horizontal arm.

The solution under investigation was poured into the tube thus prepared and then warmed up to about 40° so as to prevent the subsequent appearance of air-bubbles that might lodge in the narrow tube and separate the column of solution. The apparatus was then fixed in a stand and the end of the capillary tube sealed, and the substance intended to introduce coagulation introduced. A soft cork was inserted in the test-tube and pushed down somewhat; upon this a little mercury was poured and over the mercury a layer of melted wax. In this way evaporation of the solution was prevented. If a speed of coagulation ensued the coagulum would proceed in the horizontal tube where its progress could be measured.

EXPERIMENTS WITH COLLOID IRON SOLUTION.

The solution was prepared as described on page 376. Its analysis showed it to contain per liter 13.763 grams iron and 2.139 grams chlorine.

A tube was filled with this solution (A) and a second one with the solution diluted with twice its volume of water (B). Coagulation was started in both cases by the addition of a trace of sulphuric acid.

Solution A.—The coagulum at first nearly filled the test-tube but did not enter into the side tube; it gradually settled down so that now after twenty months it occupies the lower portion of the tube only below the mouth of the side tube. The solution

still has the characteristic red color of dissolved iron but not quite so dark as that of the stock solution. The sulphuric acid added seems to have been insufficient to enter into combination with all the iron.

Solution B.—The sulphuric acid added was sufficient to precipitate all the iron in the test-tube. The coagulum at first filled all the main tube and penetrated three millimeters into the side tube. As the coagulum settled, it left the supernatant liquid clear and colorless, while the filament of coagulated iron oxide advanced a little into the horizontal tube. In about six months the coagulum had settled below the side opening leaving a detached filament in the side tube. In the fourteen months, since, the filament has not advanced half a millimeter. Furthermore, while in the vertical tube the liquid is colorless, on the farther side of the plug of coagulated iron oxide, the solution still has a reddish color; the plug appears to act as a semipermeable membrane preventing the farther diffusion of the acid, if, indeed, all the acid has not already entered into combination.

EXPERIMENTS WITH COLLOID SILICIC ACID SOLUTIONS.

The solution of colloidal silicic acid was prepared by adding dilute hydrochloric acid to a solution of sodium silicate and dialyzing the resulting mixture until nearly free from chlorine. It was observed that if the dialysis was allowed to proceed until all chlorine detectable by silver nitrate solution had left the parchment paper tubes, the solutions generally coagulated as soon as poured into the test-tube or very soon afterwards. A small amount of chlorine, however, kept the solutions from coagulating for a long time. I have now a couple of solutions prepared as above over two years ago which apart from a very slight precipitate in the bottom of the bottles show no signs of coagulation; they are opalescent and contain a little chlorine.

An analysis of the solutions employed in ascertaining the presumed speed of coagulation resulted in 7.3276 grams silica and 0.0374 gram chlorine to the liter.

Two tubes similar to the one described on page 378 were filled with this solution and the following substances added to start coagulation: 1. Some of the solution was boiled and the crusts appearing around the edges of the dish as the water boiled away

were washed and added to the solution in the tube. 2. A portion of the silicic acid was coagulated with a little lime-water, the coagulum washed and added.

These tubes have been under observation for over twenty months and have not shown any tendency towards a spread of coagulation. Apart from an extremely slight precipitation they have the same appearance to-day as when first prepared.

EXPERIMENTS WITH SOLUTIONS OF EGG ALBUMEN.

The white of a fresh egg was cut through many times with a pair of scissors and mixed with three times its volume of water and filtered. A few drops of toluene were added to the filtrate and the whole thoroughly shaken together.

A tube was filled with this solution and some carefully washed coagulated albumen obtained by adding nitric acid to a portion of the same solution added.

The tube has been standing now for about twenty months, and no trace of a spread of coagulation is discernible. The coagulated albumen added has settled down to the bottom of the test-tube, and the solution has turned slightly yellow. There is no indication of putrefaction, however; the toluene seems to prevent that very well.

CONCLUSIONS.

The above experiments, made with solutions of colloids of quite different nature, seem to prove that coagulation started in one part of a solution does not necessarily spread through the whole body of the solution. The analogy assumed hitherto between colloid solutions and supersaturated crystalloid solutions does not seem to be more than seeming, and has no foundation in fact. It is extremely improbable that colloid solutions are comparable with supersaturated solutions.

CHICAGO, ILLINOIS, MARCH, 1898.

NEW BOOKS.

DAS OPTISCHE DREHUNGSVERMÖGEN ORGANISCHER SUBSTANZEN UND DESSEN PRAKTISCHE ANWENDUNG. BEARBEITET VON DR. H. LANDOLT, Professor der Chemie an der Universität zu Berlin. Unter Mitwirkung von DR. O. SCHÖNROCK, DR. P. LINDNER, DR. SCHÜTT, DR. L. BERNDT, DR. T. POSNER. Zweite gänzlich umgearbeitete Auflage. Mit Abbildungen. xxiv + 655 Seiten. Braunschweig: Vieweg und Sohn. 1898. Price, M. 18.

The property of certain substances, of rotating the plane of polarized light, has long been known and has been the object of much research. The practical applications of this knowledge, however, attained a high degree of accuracy and usefulness before the theory of the phenomenon was understood or any but the most superficial explanations were offered for it. The way was first opened to definite knowledge concerning the cause of the rotatory powers of chemical compounds when, in 1874, J. H. van 't Hoff, of Utrecht, and J. A. LeBel, of Paris, announced in papers, separated by only a few weeks, a new theory; *viz.*, that optical activity stood in intimate relation to chemical structure. Indeed this was the beginning of a new epoch in chemical science. In sympathy with the suddenly developed interest in the subject, Professor Landolt, then of the Polytechnic School at Aix-la-Chapelle, brought out in 1879 a modest work of 237 pages, entitled "Das optische Drehungsvermögen organischer Substanzen und die praktische Anwendung Desselben." At that time this was the only work in existence which summed up what was known on the subject. In the nineteen succeeding years no other branch of chemistry has shown greater development or offered more complete and convincing verification of a fundamental theory than that called stereochemistry. Indeed such a mass of proof has been presented that the van 't Hoff–LeBel hypothesis has been generally accepted. In this new edition of his work the author says, "The principle of the asymmetric carbon atom may be designated as one of the best established theories of chemistry."

The second edition of Professor Landolt's monograph naturally records the immense strides made in this field. The book itself has grown to 655 pages and the number of optically active bodies known in 1879, *viz.*, 300, has increased to 700, for which

the specific rotation has been calculated with more or less attention to the conditions affecting accuracy. So far as the writer is informed this still remains the only work of its kind, but no number of rivals could diminish the appreciation one feels when he realizes the immense amount of material which has been carefully digested and notes the clear and systematic form of its presentation. Even the mechanical features of the book, the paper and the clear type of different sizes which the German book-makers so successfully employ to indicate the relative values of sections and paragraphs, are in keeping with the beautiful phenomenon, and the elegant theory to which it is devoted. It is written from the chemist's standpoint with such exposition of purely physical principles as to render them intelligible to other than physicists. No important details are omitted, but it is apparent that much of doubtful authenticity has been excluded. The literature citations are quite full, and this, of course, is of great value in a book of this kind. An interesting feature is the frequent and appropriate reference to the historical features of certain theories and reactions. The practical applications made of the rotatory powers of such substances as the carbohydrates, alkaloids, camphor, etc.; descriptions of the various instruments employed in the measurement of this power with directions for their use; all receive their full share of attention.

Those who have not followed recent advances in this field will find here admirable summaries of researches and important generalizations not otherwise accessible except as diffused through journals. It is of interest to learn that while in 1879 only four substances were known to exist in different optical modifications, *viz.*, tartaric acid, maleic acid, camphor, and camphoric acid, now over one hundred are recorded, of which most are known in the laevo, dextro, and inactive forms. Interesting sections are devoted to the formation and separation of racemic compounds, describing the methods used with such fruitful results by Fischer, Liebermann, Ladenburg, Lewkowitsch, Frankland, and others. Considerable space is devoted to the discussion and summing up of our knowledge of multirotation, the puzzling phenomenon concerning which many theories have been advanced and none accepted. Professor Landolt expresses himself to the effect that it is settled that the cause of multirota-

tion of sugars is to be found in the existence of isomeric modifications which in aqueous solutions are transformed (*umgewandelt*) the one into another.

The chief divisions of the work are six; *viz.*, I. General Discussion of Optical Activity; II. Physical Laws of Circular Polarization; III. Specific Rotation; IV. Apparatus and Methods for Determining Specific Rotation; V. Practical Applications; VI. Rotation Constants of Active Bodies.

The work is admirable from every standpoint and will be indispensable to the chemist or physicist who hopes to maintain footing in this important field. W. E. STONE.

SPECTRUM ANALYSIS. By JOHN LANDAUER, LL.D.; authorized English edition by J. BISHOP TINGLE, PH.D., F.C.S. New York: John Wiley & Sons. x + 239 pp. Price, $3.00.

This is the translation of Dr. Landauer's article in Fehling–Hell's Handwoerterbuch, which has been republished as a separate book. Dr. Tingle recommends it as a text-book for American students of chemistry.

While commending the book to the attention of chemists already familiar with the principles of spectroscopy, the reviewer does not think it adapted to the use of beginners. No connected directions are given for the adjustment and use of the spectroscope and spectrometer; not even a diagram showing the use of the various parts; no suggestions for practice in the identification of lines or detection of elements. In fact, the attention of the writer is mainly directed to work that requires the most expensive apparatus and practiced manipulation. While use is made, from the outset, of such terms as "D line," "K line," etc., we must proceed to Chapter IX, before reaching a cursory account of Fraunhofer's notation. In the introductory discussion of the properties of light, no attempt is made to connect the refractive index with λ: consequently "dispersion" must be treated aphoristically. Total reflection is ignored: consequently the third tube of the spectroscope remains an enigma. By neglecting interference, diffraction is explained so obscurely, that the subsequent exposition of Prof. Rowland's work would be incomprehensible, without outside help. Practical applications of spectroscopy, that would interest the chemist, rather than the astronomer, fare badly. The two lines devoted to forensic ex-

amination and the four which mention the spectroscopic control of the Bessemer, could not have been found without the index.

All of this merely proves that a cyclopedia article cannot do duty as a text-book, and it is to be hoped that the first five chapters will be recast for subsequent editions. The latter part of the work shows admirable industry in the collation and recalculation of material, and good judgment in the elimination of superseded and unsatisfactory data. Exception might be taken to the omission of Michelson's work with the refractometer, of reference to hypotheses concerning fluorescence, and of discussions over atom-spectra and molecule-spectra. On the other hand, praise must be given to the lucid and impartial exposition of researches into the mathematical relations of spectral lines and their connection with chemical properties, as well as to the discussion of solar and astral spectra. It would be a valuable addition to the reference library of every chemist.

Dr. Tingle's translation is easy and idiomatic, the only solecisms being the persistent use of 'discovery,' for 'Erfindung,' and of the indefensible term 'magnetic current,' on page 75.

MORRIS LOEB.

ON LABORATORY ARTS. By RICHARD THRELFALL, M.A., Professor of Physics in the University of Sydney. New York: The Macmillan Co. 1898. xii + 338 pp. Price, $1.50.

The rather indefinite title of this book and the purpose for its existence, may be explained by quoting from the preface: "It is true that in a well-appointed laboratory, where apparatus is collected together in greater or less profusion, the appeal is often indirect, and to a student carrying out a set experiment with apparatus provided to his hand, the temptation to ignore the mechanical basis of his work is often irresistible. It often happens that young physicists are to be found whose mathematical attainments are adequate, whose observational powers are perfectly trained, and whose general capacity is unquestioned, but who are quite unable to design or construct the simplest apparatus with due regard to the facility with which it ought to be constructed. .... It is the object of the following pages to assist the young physicist in making his first steps towards acquiring a working knowledge of 'laboratory arts.'"

The book is divided into four chapters, and the material con-

tained therein may be judged from the titles: Hints on the manipulation of glass and on glass-blowing for laboratory purposes, with an appendix on the preparation of vacuum tubes for the production of Professor Röntgen's radiation; glass-grinding and optician's work; miscellaneous processes; electroplating and allied arts, with an appendix on platinizing glass.

About one-third of the book is devoted to the many different manipulations of glass, as the use of blowpipes, glass-blowing, welding, grinding, fusing electrodes into glass, etc., in which the directions are, for the most part, clear and concise. Many of the methods offered differ from those already published, and with few exceptions only those methods are given which have met with success in the author's hands. This is more or less true of all processes given in the book. The appendix to Chapter I is a concise treatise on the preparation and the exhaustion of tubes for the production of Röntgen rays, the making of terminals and mercury pumps.

In the preface it is stated that "physical research is too difficult in itself, and students' time is too valuable, for it to be remunerative to work with insufficient appliances," but in spite of this, the greater part of Chapter II is devoted to lens-grinding, certainly a time-consuming operation, and which can hardly be classed as a laboratory art. In this chapter are also directions for making mirrors of glass and speculum metal.

Chapter III is devoted to such generally useful subjects as coating glass with aluminum and gold, cutting rock sections and sections of softer substances, soldering, etc. Thirty pages of this chapter are devoted to an excellent treatise on the preparation and properties of quartz fibers, and fifty pages to electric insulators and the properties and value of many substances used as insulators.

For the most part the directions throughout the book are well stated and to the point. An exception to this, however, is on the preparation of solutions for silvering mirrors (p. 151) in which the statement is awkward and unnecessarily involved. It is much to be regretted that a uniform system of measurement has not been adopted. Inches and millimeters, degrees Fahrenheit and Centigrade, are indiscriminately used. The index is well arranged and complete. HENRY FAY.

THE ARRANGEMENT OF ATOMS IN SPACE. BY J. H. VAN 'T HOFF. Second revised and enlarged edition, with a preface by JOHANNES WISLICENUS, and an appendix, Stereochemistry among Inorganic Substances, by ALFRED WERNER. Translated and edited by ARNOLD EILOART. London, New York and Bombay: Longmans, Green & Co. Cloth. xi + 211 pp. Price, $1.75.

The writer recalls the amusement with which a modest brochure, entitled "La chimie dans l'Espace," was received in the leading laboratories of Europe, twenty years ago. Pleasantries, however, soon gave way to serious discussion, and that in turn was shortly followed by a widespread acceptance of the somewhat startling hypothesis of the young and comparatively unknown author, Professor J. H. van 't Hoff, of Amsterdam. Now he is recognized by all as the founder of what we term stereochemistry, and as having introduced into our science a concept as brilliant and daring as the theories which are associated with the names of Dumas, Laurent, Gerhardt, Kekulé, or Mendeléeff.

The present volume will be welcomed by the teaching profession as a standard text-book on stereochemistry. It presents all that is necessary for a student, in brief, compact form, and exhibits throughout the lucidity so characteristic of van 't Hoff's writings.

The historical portion is short and the question of priority with LeBel is handled in a courteous manner which does full justice to the talented French chemist. In the seven chapters devoted to carbon compounds, four are given to those containing one or more asymmetric carbon atoms, one to substances of the ethylene type, one to ring formation, and one to the important subject of the numerical value of the rotatory power. The presentation of theory and of experimental evidence is well balanced, while the lists of compounds involved are tabulated in a very clear and helpful manner. Points of existing controversy are fairly stated, and the author abstains from polemics. The fulness of bibliographic references and of the tabular statements is such, that the work rises notably above the level of a text-book and, despite its small size, can effectively replace Bischoff's large "Handbuch der Stereochemie." This result is attained in a great measure by a condensation of formulas. To a certain extent this practice is of doubtful advisa-

bility. The book will naturally be placed in the hands of comparatively young chemists. No device tending to bring out and emphasize the peculiar relations of the asymmetric carbon atom, should be neglected, at least in the early chapters. The use of a one-line formula, such as $CO_2HCHOHCH_2CO_2H$, while amply sufficient for the more advanced student, is to be deprecated at the beginning of the book. The additional space required for more ample graphic formulas, would be advantageously used from the standpoint of the teacher.

The chapter on the stereochemistry of nitrogen compounds is comparatively brief, as van 't Hoff's interest in this branch is less pronounced. The most recent results are, however, carefully summarized.

An appendix contains a note by Professor Werner on the stereochemical isomerism of inorganic compounds, confined, of course, to the amines of cobalt and platinum.

Dr. Eiloart has furnished an excellent translation and added in a few instances pertinent notes, introducing the results of recent investigations. It is a question whether the use of *right-handed* and *left-handed* for *dextro-rotatory*, etc., is to be recommended. A simpler expression for the Latin derivatives is undoubtedly desirable; but the introduction of the word *hand* recalls the Greek idiom, "bare-headed as to the feet," and certainly does not simplify the nomenclature.

Typographical errors are rare, but occasionally meet the eye, as in the formulas of malic and lactic acids, pages 29 and 163.

THOMAS H. NORTON.

BIBLIOGRAPHY OF THE PLATINUM GROUP, 1748–1896. By JAMES LEWIS HOWE. Smithsonian Miscellaneous Collections, No. 1084. 8vo. pp. 318.

This forms a very valuable contribution to chemical bibliography, and will prove an indispensable aid to all workers in the field of the platinum metals. A glance at this volume is sufficient to show the great amount of labor expended upon it by Dr. Howe, and a closer examination will prove how faithfully and conscientiously the work has been done. Over one hundred sets of journals were consulted in its preparation, besides a large number of books, pamphlets, and single copies of periodicals. The total references number nearly 2500. They are first

arranged by years with the name of the author, followed by the title of the paper. Instead of a continuous consecutive numbering, however, the numbering is broken by each year and is consecutive for that year only. Nearly fifty pages are filled with a subject index in which the references are divided under sixty-six different headings. This makes the book particularly useful to a worker in any special field. An author index, filling some fifteen double-columned pages, completes the book.

Chemists owe a debt of gratitude to Dr. Howe for this tedious yet most helpful work, which he has so ably completed, and to the Smithsonian Institution for rendering its publication possible.

F. P. VENABLE.

THE CALORIFIC POWER OF FUELS. Founded on Scheurer-Kestner's Pouvoir Calorifique des Combustibles, with the addition of a very full collection of tables of heats of combustion of fuels, solid, liquid, and gaseous, to which is also appended the report of the committee on boiler tests of the American Society of Mechanical Engineers (December, 1897); table of constants used. By HERMAN POOLE, F.C.S. New York: John Wiley & Sons. 1898. xv + 255 pp. Price, $3.00.

The general character of the book is pretty well indicated by the somewhat lengthy title. The first six chapters of the book are given, mainly, to a description of the various forms of calorimeters in common use for the determination of the heating power of fuels. The descriptions are satisfactory and include brief directions for the use of the more important forms of apparatus and an account of the corrections to be applied. Chapters VII to IX discuss solid, liquid and gaseous fuels chiefly from the standpoint of heating effect. Then follow three chapters devoted to the subject of boiler tests and the necessary determinations and calculations, especially those relating to loss of heat in waste gases. The Appendix includes the report of the committee on boiler tests referred to in the title, and very full tables, especially of the heating power of coals from all parts of the world. Unfortunately these tables, which the author appears to consider especially valuable, contain internal evidence that some of the values given are worthless. Thus, on page 216, three determinations for the same coal are given, with a difference of twenty-five per cent. between the highest and lowest values. Also, although most of the values are on the basis of

the coal burned to liquid water, in one case, at least, results which were published in terms of the fuel burned to vapor of water are given without the necessary correction. On page 106 analyses of natural gas are given which represent it as containing large amounts of hydrogen, although Professor Philips has, apparently, demonstrated[1] that this gas is never present. In the same table marsh gas and methane are given as though they were different substances. The value of the tables would be greatly increased if exact references to the source of the data were given.

While it is evident that the tables must be used with care and discrimination, the book will prove a useful one to engineers and chemists interested in the subject of fuels.

W. A. NOYES.

METHODS FOR THE ANALYSIS OF ORES, PIG IRON, AND STEEL. Easton, Pa.: The Chemical Publishing Co. 1898. 8vo. 131 pp. Price, $1.00.

This well printed and neatly bound volume contains a symposium of methods of iron analysis, in use in the laboratories of iron and steel works in the region about Pittsburg, Pa., together with an appendix containing various special methods of analysis of ores and furnace products. The methods are given in detail by the chemists in charge of the fifteen laboratories represented and may be considered to represent the general practice of the chief iron and steel works in the principal center of the iron industry in the United States. When one reflects upon the vast commercial and manufacturing interests that are based upon the results of these methods of analysis, they become well worth careful study and comparison by every one interested in iron analysis.

P. W. SHIMER.

TEXT-BOOK OF PHYSICAL CHEMISTRY. By CLARENCE L. SPEYERS. iv + 224 pp. New York: D. Van Nostrand Co. Price, $2.25.

There is a deplorable lack of continuity in the teaching of science between our universities and the schools preparing for them. While the student continues his study of languages and mathematics on entering college, he generally begins his study of science over again. Many students have had good courses in physics and chemistry in the secondary schools and are fitted to go on with that work in college. To such students as these,

[1] *Am. Chem. J.*, 16, 406.

as well as to those who may elect elementary courses in physical science during the first year or so of college, it seems highly desirable to offer a course in elementary physical chemistry. There is a vast body of knowledge lying between physics and chemistry which is of great interest and importance; it has in the main been obtained by what may be termed advanced methods, but its results can be advantageously presented in elementary form. A course presenting these results and the outlines of the methods employed in getting them seems a desideratum. Such a course would prove to be very profitable and beneficial; it would be an excellent "culture course" for those making physical science a minor subject, and a good preparatory course for those taking physics or chemistry as a major. It is a mistake to believe that the study of physical chemistry can be taken up with advantage only after a considerable acquaintanceship with the facts and theories of physics and chemistry has been made; the elements of these sciences are quite sufficient for a good comprehension of elementary physical chemistry. To insure the success of such a course, a text-book on physical chemistry corresponding in difficulty to our best elementary text-books on physics or chemistry is needed. The reviewer had hoped that the book at hand would fill this need, but finds it suited for quite advanced students only; and the need still exists.

This book represents what "the author" has been "in the habit of teaching the senior class in the chemical course in Rutgers College," and "is intended for self-instruction as well as classroom use." "The view that matter is a collection of energies in space" has been adopted; this view, due to a particular German school of physical chemists, gives the book throughout a peculiar complexion. Thus, on page 4 is found: "In ordinary chemical language we say chemical reaction takes place between definite weights of matter. In our language we should say the relation between the intensities of the distance energies (gravity energies) of two or more collections reacting to form another definite collection, is fixed." Another sample of the "energetic" style is this: "when the intensity of the heat energy is not relatively high, the intensity of volume energy is inversely proportional to the capacity only when the intensity of the volume energy is low," (p. 28) which probably means that

at low temperatures and high pressures gases do not obey Boyle's Law.

The author states (p. iv): "With Ostwald, I feel convinced that the materialistic interpretation has passed its prime and has no promise for the future." This is an extreme and one-sided view. Careful study of Boltzmann's writings cannot fail to convince the fair and conscientious reader, no matter how biased he may be, that materialistic conceptions are necessary and useful; and as for their help in discovering new truths, reference need only be made to the splendid confirmations by Zeemann, of Lorentz's atomistic views and theories.

The author goes further even than Ostwald in his classification of the kinds of energy. Chemical energy he rejects, because (p. 177) "the assumption of chemical energy is strictly gratuitous and not to be advised at all;" but he makes up for this by adding internal energy, magnetic energy, and three kinds of radiant energy; *viz.*, radiant heat energy, radiant light energy, and Roentgen ray energy. It seems rather strange that he has not added *mental* energy.

The book is something more than a text-book; it is also an essay having for theme the dethronement of matter and the crowning of energy.

Some of the author's definitions are far from being clear and logical. For instance, "a chemical change is one in which the nature of the original body is very much changed," while "a physical change is a change which does not alter the characteristic chemical nature of the body." This amounts to saying: A change is a change or alteration; a chemical change is a big change, while a physical change is a little alteration.

An original feature of the book is the introduction of numerous problems; most of these are excellent and help greatly towards elucidating the text. A curious illustration of how facts may be made to fit theories is the following: The author in one of his problems (p. 81) assumes data given by the reviewer to be accurate enough to warrant the conclusion that "the benzene molecule seems to be polymerized nearly three times," while Bancroft (The Phase Rule, p. 118) thinks the same data to be at least ten per cent. in error. Both establish their theories, however.

The style of the book is concise and a mathematical treatment predominates. The historical development of any subject is avoided so that the reader hardly knows to whom he may attribute certain views advanced, by no means current among physical chemists. This avoidance of the historical treatment detracts much from the value of the book, for in such a subject where there still exists a conflict of views on many points, the only satisfactory treatment is the historical.

The statement of the author (p. iv) that "whoever works through" the book "conscientiously, paying particular attention to the problems, will get a very fair idea of physical chemistry," is, in the opinion of the reviewer, unwarranted. What the reader will get is a knowledge of a lot of subtle distinctions about energy, some practice in the handling of mathematical equations, and an incomplete acquaintance with some physico-chemical laws. But a "fair" idea of physical chemistry he certainly will not get.

C. E. LINEBARGER.

BOOKS RECEIVED.

Spectrum Analysis. By John Landauer, LL.D. Authorized English edition by J. Bishop Tingle, Ph.D., F.C.S. New York: John Wiley & Sons. 1898. x + 239 pp. Price $3.00.

The Sugar Beet in Illinois. Bulletin No. 49. University of Illinois, Agricultural Experiment Station, Urbana, Ill. 1898. 52 pp.

The Cost of Production of Corn and Oats in Illinois in 1896. Bulletin No. 50. University of Illinois, Agricultural Experiment Station, Urbana, Ill. 24 pp.

An Ephemeris of Materia Medica, Pharmacy, Therapeutics and Collateral Information. Vol. V, No. 1. January, 1898. By Edward R. Squibb, Edward H. Squibb, and Charles F. Squibb. Brooklyn, N. Y. 1898. 176 pp.

Preparation and Application of Fungicides. Bulletin No. 25. Connecticut Agricultural Experiment Station, New Haven, Conn. 1898. 16 pp.

On the Crystalline Structure of Gold and Platinum Nuggets and Gold Nuggets. By A. Liversidge, LL.D., F.R.S., Professor of Chemistry, University of Sydney, N. S. Wales. 10 pp. 16 plates.

On Some New South Wales and Other Minerals. On the Amount of Gold and Silver in Sea-water. The Removal of Gold and Silver from Sea-water by Muntz Metal Sheathing. By A. Liversidge, M.A., F.R.S., Professor of Chemistry, University of Sydney, N. S. Wales. 42 pp.

Abbreviated Names for Certain Crystal Forms. Models to Show the Axes of Crystals. By A. Liveridge, M.A., F.R.S., Professor of Chemistry, University of Sydney, N. S. Wales. 10 pp.